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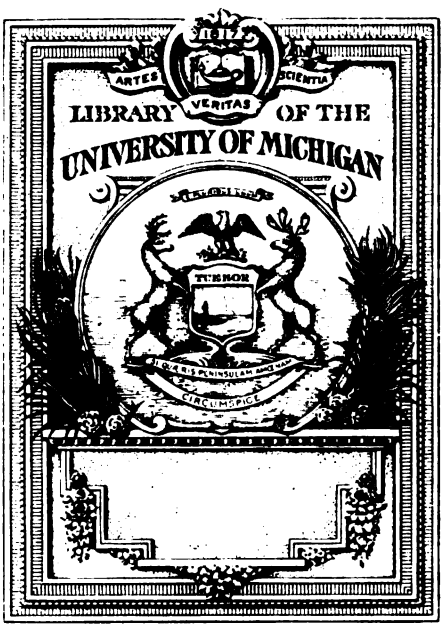
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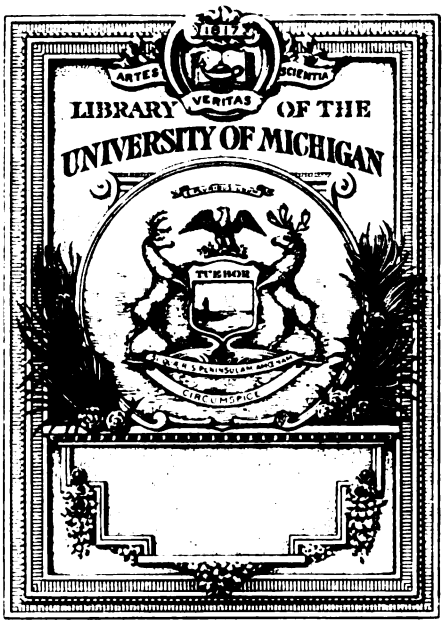
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THE

CHEMISTRY OF ESSENTIAL OILS

AND ARTIFICIAL PERFUMES

BY

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PREFACE TO THE SECOND EDITION.

THE present edition has been brought up to date, and covers the most recent researches in this important domain of chemistry.

The chapter on Terpeneless Oils has been omitted, as the subject does not appear to be of sufficient importance for detailed treatment.

The constant inquiries received by the author as to whether given oils satisfy the requirements of foreign Pharmacopœias have justified the addition of an appendix giving the requirements of the principal Pharmacopœias.

Many new facts will be found quoted in regard to certain essential oils, which are completely at variance with the views commonly held at the time the last edition was published. A consideration of such facts will emphasise the importance of carefully watching the variation in the properties of essential oils produced by change in soil, climate and general conditions of growth. It is only by such continual experience that an accurate opinion as to the purity of certain oils can be arrived at. Typical examples of this will be found under Rosemary, Spike-Lavender and Linaloe Oils.

257843

The rapid growth in our knowledge of this group of natural products will, in the author's opinion, be considered ample justification for the publication of a new edition of this work.

ERNEST J. PARRY.

THANET HOUSE,
56A GREAT DOVER STREET,
LONDON, S.E., *September*, 1908.

PREFACE TO THE FIRST EDITION.

THE developments in the chemistry of essential oils have been so rapid and so extensive during the past few years, that I need make no apology for the appearance of the present work, in which I have attempted to group together the more important of the published facts connected with the subject. No attempt has been made, in the chapters dealing with the preparation and analysis of essential oils, to do more than give an outline of the principles involved, as, in the first place, each subject could well occupy a volume by itself, and in the second place, no man with mere text-book knowledge would undertake either branch of the subject in a practical manner. The treatment of the essential oils systematically has necessitated the suppression of much doubtful and disputed work, and whilst great care has been taken to keep the facts up to date, it has been necessary to only touch slightly on a good deal of quite recent disputed work, which must be regarded as still in an unsettled condition.

My thanks are due to a number of friends who have rendered me much assistance during the preparation of the volume; especially to Mr. J. H. Coste, F.I.C., who has rendered much help in the

revision of the proof sheets, and Mr. H. F. Lambert, who has assisted me in the preparation of the sketches. I have also to thank the editor of the *Chemist and Druggist*, Messrs. Townson & Mercer and Messrs. Schimmel & Co., for the loan of blocks and permission to reproduce several illustrations; and Mr. Heinrich Haensel, Messrs. Stafford, Allen & Co., and Messrs. Sparks, White & Co., for generously placing numerous samples at my disposal.

ERNEST J. PARRY.

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CHAPTER I.

THE GENERAL PROPERTIES OF ESSENTIAL OILS.

An absolutely scientific definition of the term *essential* or *volatile* oils is hardly possible, but for all practical purposes they may be defined as odoriferous bodies of an oily nature obtained from vegetable sources, generally liquid (sometimes semi-solid or solid) at ordinary temperatures, and volatile without decomposition. This definition must be accepted within the ordinary limitations which are laid down by the common acceptation of the words, which will make themselves apparent in the sequel, and show that no more restricted definition is either advantageous or possible. Many essential oils, for example, are partially decomposed when distilled by themselves, and some even when steam distilled.

The volatile oils occur in the most varied parts of the plant anatomy, in some cases being found all over the various organs, in others being restricted to one special portion of the plant. Thus in the conifers, of which the pine is a type, much volatile oil is found all over most parts of the tree; whereas in the rose, the oil is confined to the leaves of the flower; in the cinnamon, to the bark and the leaves, with a little in the root; in the orange family, chiefly to the flowers and the peel of the fruit; and in the nutmeg, to the fruit. The functions of these bodies in the plant economy are by no means well understood. Whilst it is easy to understand that a fragrant odour in the unfertilised

flower may be of great value in attracting the insects with the fecundating pollen, this can have no bearing on the occurrence of odorous bodies in, say, the bark or internal tissues. At present one is compelled to class the majority of the essential oils as, in general, belonging to the by-products of the metabolic processes of cell life, such as are many of the alkaloids, colouring matters and tannins; with, possibly, in certain cases, excretionary functions. The structures of the plant which carry the secreted oils occur in the fibro-vascular as well as in the fundamental tissues. Dependent on their mode of origin, the receptacles may be either closed cells containing nothing other than the matter secreted, or they may be vascular structures which have their origin in the gradual absorption of adjacent cell walls, and the consequent fusion of numerous cells into one vessel; or, again, they may be intercellular spaces, large cavities formed in two distinct ways, (1) by the decomposition of a number of adjacent cells, leaving a cavity in their place, whose origin is thus *lysigenous*, (2) by the separation of adjacent cell walls without injury to the cells themselves, thus leaving a space for the secretion, whose origin is *schizogenous*. Sometimes the oils contain a non-volatile resin in solution, forming an oleoresin. For example, isolated cells containing an oleoresin are found in some of the Laurineæ, Zingiberaceæ and Coniferæ, and intercellular spaces (the so-called *glands*) in some of the Umbelliferæ and Coniferæ.

Charabot, in conjunction with his pupils and with Bertrand, has carried out numerous investigations with a view to showing what is the process governing the formation of essential oils in plants, and, to some extent, what are their functions. Whilst the author considers many of Charabot's generalisations are not sufficiently supported by experimental fact, it appears proper to give an outline of the more important of them. From a comparative examination of the plants of

Ocimum basilicum (the sweet basil) at various stages of their development, they come to the following conclusions. The author is indebted to Messrs. Schimmel & Co. for a portion of these results.

During the period which precedes the appearance of the first inflorescences, the green parts of the plant contain a comparatively soluble oil which is poor in methyl-chavicol, but rich in terpenes and their derivatives. The first inflorescences contain a less soluble oil, richer in methyl-chavicol. It appears that during the formation of a new oil rich in terpene derivatives in the young shoots, a portion of these terpene compounds is consumed in the inflorescences. When the flowering period has nearly come to an end, the quantity of the oil in the green parts diminishes, and with it its solubility; but in the inflorescences the quantity of oil increases. A readily soluble portion of the oil, which is first of all present in the leaf, passes into the twig by osmosis, and thence reaches the blossom, where organic substances are required for the processes of fertilisation and the accumulation of reserve substances. When the osmotic pressure in the blossom decreases owing to the consumption or excretion of organic bodies, a transfer of metabolic substances takes place from the leaf to the blossom. The solubility of the oil of the inflorescences does not increase, as the solubility of the oil contained in the entire plant decreases owing to a reduction in its content of terpene derivatives. From this it follows that the latter are partly consumed in the blossom. Later on, when the blossom has performed its function, and the fruit is ripe, it is found that the oil in the green parts of the plant increases, and becomes more soluble by increase of the terpene derivatives, whilst it diminishes in the inflorescences. It would therefore appear that the oil to some extent passes back into the green parts of the plant.

They also consider that the process of fecundation and

fructification consumes a considerable amount of the essential oil, or of the substances from which the oil is immediately evolved. They give the following table showing the difference in the composition of the essential oils from the two series of plants.

	Test Plants.		Deprived of Inflorescences.	
	From Green Plants. Per cent.	Flowers. Per cent.	From Green Plants. Per cent.	Flowers Removed. Per cent.
Estragol . . .	67·5	29·7	68·4	42·3
Linalool . . .	20·4	29·9	24·7	33·4
Other terpene bodies .	12·1	40·4	9·9	24·3

Bertrand Fils have made studies on the formation and distribution of the essential oil and on the gradual distribution of the terpene compounds in the various organs of the plant. The experimental plant was in both cases *Artemisia absynthium* L. The experiments showed that the essential oil is present in abundance in the plant which is yet quite young. Up to the time of inflorescence the amount of essential oil increases. But then a decrease in the percentage, as well as in the absolute quantity of oil, takes place. This quantity of oil is used up when after the flowering period the act of fertilisation is accomplished. Although it is possible that during this period a new formation of odorous substances takes place, it is not equal to the quantity consumed. The conclusion drawn by Bertrand Fils from the results obtained is this, that the essential oils in the plant are the substances which are used up in the organism in order to ensure the continuance of the species. They show that the root of the young wormwood shrub does not contain any oil, the stalk comparatively little, but that the leaf contains the bulk. At the commencement of the flowering period the oil makes its appear-

ance in the root, where its percentage increases steadily, also its absolute weight. The loss of essential oil which can be demonstrated during the development of the fruit, is borne by the leaves, stalks and inflorescences. With regard to the distribution and development of the terpene compounds in the organs of the plant, the examination included the comparative determinations of the essential oil present in the individual organs, as well as the solubility of the constituents. A long time before the first inflorescences make their appearance, the essential oil of the plant only contains traces of thujone; the oil of the stalks is less soluble than that of the leaves. Immediately after the first inflorescences, the oil contained in these also shows a lower solubility than the oil of the leaves. The ester-content is largest in the roots, and smaller in the stalks, inflorescences and leaves. The content of free thujyl alcohol does not differ largely in the various organs of the plant. Thujone is chiefly present in the leaves, and only traces of it are found in the stalks.

Most of the oils occur free in the plant tissues, but occasionally they do not exist as such in the living organism, but result from the decomposition of a compound existing in the tissue, by means of a ferment in the presence of water. Examples of this are the essential oils of almond and of mustard. In the former case, the oil results from the decomposition of the glucoside amygdalin by means of the ferment emulsin, and in the latter from that of the glucoside potassium myronate by means of myrosin, water being essential in both cases.

The physical properties of the essential oils are as varied as the sources from which they are obtained. Not only is their different nature dependent on the plant from which they are obtained, but a change of soil and climate will often cause enormous difference in the essential oil yielded by the same plant. Such is most markedly the case with lavender,

peppermint, and roses. As an example, the first plant may be quoted. The oil distilled from plants grown at Mitcham in Surrey never contains more than about 7 to 10 per cent. of the compound, linalyl acetate, whereas the same plant, *Lavandula vera*, growing in the south of France, frequently contains over 35 per cent. of the same body.

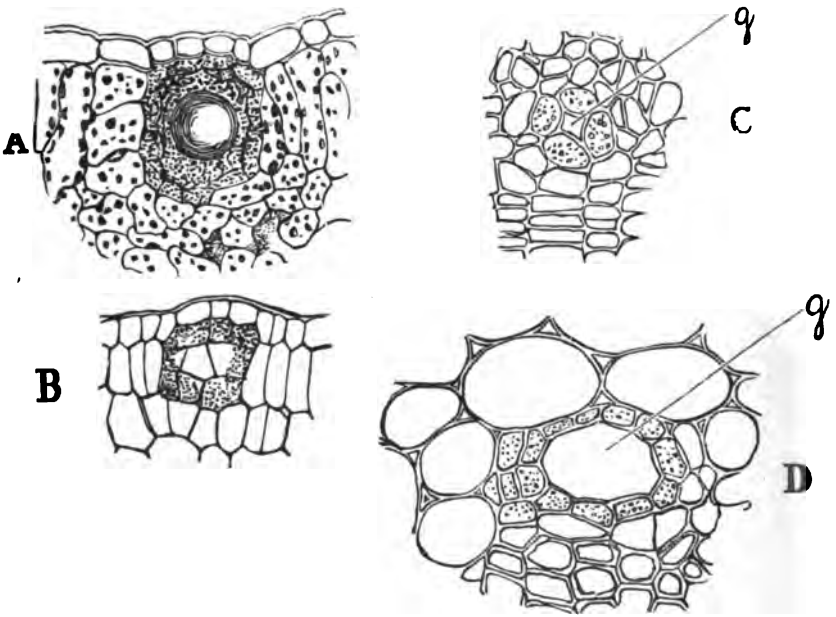


FIG. 1.

In the above diagram A represents an oil cavity below the upper surface of the leaf of *Dictamnus Fraxinella* (× 320). B represents the same in an early stage, and shows the mother cells of the cavity before their absorption (lysigenous). C is an early and D a later stage of the formation of a resin passage in the young stem of the Ivy (*Hedera Helix*) (× 800). In both cases *g* shows the separating cell (schizogenous).

And Mitcham plants, transplanted to the south of France, yield an oil which approximates more and more to the ordinary French oil, according to the time they have been growing under their new conditions of life.

In general, the volatile oils are practically insoluble in water, although the traces which go into solution are sufficient to render the water highly odoriferous. They are, however, soluble in most organic solvents. Their density varies from much below to much above that of water. A few consist almost entirely of one definite compound, such as oil of wintergreen, which is nearly pure methyl-salicylate, but the majority are mixtures of several different bodies. They are mostly inflammable liquids, distilling undecomposed under ordinary atmospheric pressure. A few, however, undergo some decomposition, and must be distilled under reduced pressure, or with steam. Many of them are very susceptible of change, which is chiefly brought about by oxidation by means of atmospheric oxygen. In order to preserve such oils, they must be kept in dark, cool places, protected from the action of the air.

The optical properties of essential oils are very characteristic. They invariably possess very high refractive indices, usually from 1·45 to 1·56, and most of them have the property of rotating the plane of polarisation. The application of this property forms one of the most useful criteria in judging of the purity of a given sample of oil, and will be treated in detail in the sequel. The following table, published by Dr. Gladstone some thirty years ago (*Jour. Chem. Soc.*, xvii., p. 3), is of interest in this respect, although some of the actual figures must be rejected on account of the obvious adulteration of the samples, and the table may to a certain extent be regarded as of only historical value. The rotation figures are expressed for a column of ten inches of liquid :—

Oil.	Specific Gravity at 15·15°.	Refractive Index for the D line at Temperature quoted.		Rotation.
Aniseed	·9852	16·5°	1·5566	− 1°
Bay	·8808	18·5°	1·5022	− 6°
Bergamot	·8825	22°	1·4625	+ 23°
,, (Florence)	·8804	26·5°	1·4614	+ 40°
Birch Bark	·9005	8°	1·4921	+ 38°
Cajuput	·9203	25·5°	1·4611	0
Caraway	·8845	19°	1·4671	+ 63°
Cassia	1·0297	19·5°	1·5748	0
Cedar	·9622	29°	1·5035	+ 3°
Citronella	·8908	21°	1·4659	− 4°
Cloves	1·0475	17°	1·5312	− 4°
Coriander	·8775	10°	1·4652	+ 21° (?)
Cubebs	·9414	10°	1·5011	—
Dill	·8922	11·5°	1·4834	+ 206°
Elder	·8584	8·5°	1·4749	+ 14·5°
Eucalyptus amygdalina	·8812	13·5°	1·4788	− 136°
,, oleosa	·9322	13·5°	1·4718	+ 4°
Indian geranium	·9043	21·5°	1·4714	− 4°
Lavender	·8908	20°	1·4648	− 20°
Lemon	·8498	16·5°	1·4727	+ 164°
Lemon-grass	·8932	24°	1·4705	− 3° (?)
,, (Penang)	·8766	13·5°	1·4837	0
Mint	·9342	19°	1·4840	− 116°
,,	·9105	14·5°	1·4822	− 13°
Myrtle	·8911	14°	1·4680	+ 21°
Neroli	·8789	18°	1·4676	+ 15°
,,	·8743	10°	1·4741	+ 28°
Nutmeg	·8826	24°	1·4709	+ 44°
,, (Penang)	·9069	16°	1·4818	+ 9°
Orange peel	·8509	20°	1·4699	+ 32° (?)
,, (Florence)	·8864	20°	1·4774	+ 216°
Parsley	·9926	8·5°	1·5162	− 9°
Patchouli	·9554	21°	1·5050	—
,, (Penang)	·9592	21°	1·5040	− 120°
,, (French)	1·0119	14°	1·5132	—
Peppermint	·9028	14·5°	1·4670	− 72°
Petitgrain	·8765	21°	1·4600	+ 26°
Rose	·8912	25°	1·4627	− 7°
Rosemary	·9080	16·5°	1·4688	+ 17°
Sandalwood	·9750	24°	1·5021	− 50°
Thyme	·8843	19°	1·4754	—
Turpentine	·8727	13°	1·4732	− 79°
Verbena	·8812	20°	1·4870	− 6°
Wintergreen	1·1423	15°	1·5278	+ 3°
Wormwood	·9122	18°	1·4688	—

The composition of the essential oils is as variable as are their physical properties, and the next chapter will be devoted to a study of the more important groups of chemical

compounds which occur in them. Many of them contain several liquid ingredients, but some are solutions of solid bodies in liquids. These will frequently deposit the greater portion of the solid on being exposed to a low temperature. When this is the case, the solid is frequently referred to as the *stearoptene*, and the liquid as the *oleoptene*. These terms, however, have now no scientific meaning. After these introductory remarks we may now pass on to a detailed account of the more commonly occurring compounds in the essential oils, and thence to a study of the special oils themselves.

CHAPTER II.

COMPOUNDS OCCURRING IN ESSENTIAL OILS.

THE old terms *fatty* and *aromatic* as applied to chemical compounds have gradually given way to the more scientifically correct aliphatic and cyclic, as it has been found that many of the highly odoriferous bodies do not belong to the benzene series of compounds. The cyclic compounds are subdivided into the carbocyclic group, in which the closed chain consists entirely of carbon atoms, and the heterocyclic group, in which other atoms than carbon may be present. The bodies described here will therefore be classified according to their possessing a closed carbon chain in the molecule or not. The groups whose members are frequent constituents of essential oils are: (1) the terpenes, (2) camphor compounds, (3) the geraniol series, (4) benzene compounds, (5) open chain or aliphatic compounds other than (3).

I. THE TERPENES.

No compounds are of more frequent occurrence in essential oils than are those belonging to this important group. Very many have been described by different chemists, but a systematic study undertaken by Wallach has reduced these to a comparatively few, the best defined of which are those described below. They are, with one exception, volatile liquid hydrocarbons of the formula $C_{10}H_{16}$. Whilst agreeing closely in many of their properties, their chemical differences are sufficient to enable them to be sharply differentiated. The well-defined terpenes are: *pinène, camphene, limonene,*

dipentene, fenchene, sylvestrene, carvestrene, phellandrene, terpinolene, terpinene, thujene and *sabinene*, and, possibly, *firpene*. In addition to these there are several less known, but well-defined terpenes, which will be referred to as occasion requires, and the so-called aliphatic terpenes, of which myrcene is the type.

Pinene.—This hydrocarbon occurs in both the dextro- and the laevo-rotary form in nature. It has been described at various times as *terebenthene, australene, eucalyptene, laurene, olibene* and *massoyene*, all of which, however, were more or less impure pinene.

The active varieties of pinene are prepared by fractional distillation of a number of essential oils. American turpentine is the chief source of dextro-pinene, and French turpentine of laevo-pinene. It is found in a great many essential oils, in both forms, references to which will be found under the oils themselves. Optically inactive pinene does not occur in nature, but can be prepared by heating pinene nitrosochloride with aniline. Its properties, according to Wallach (*Ann. Chem.*, cclii., p. 132, and cclviii., p. 343), are as follows: an optically inactive liquid, boiling at 155° to 156°, of specific gravity ·858 at 20°; refractive index for the *d* line 1·46553 at 21°. The purest forms of active pinene prepared agree closely in their properties with the above, except that their optical activity is about + 40° or − 40°. When acted upon by hydrochloric acid gas, pinene yields a monohydrochloride $C_{10}H_{16}HCl$, in crystals melting at 125° and boiling at 207° to 208°, known as artificial camphor.[1] It is extraordinary that the hydrochloride prepared from *dextro*-pinene is *inactive* (*Gazz. Chim.*, 1888, p. 223), whilst that from *laevo*-pinene is strongly laevo-rotary. By abstracting the molecule of hydrochloric acid, by means of sodium acetate and acetic acid, the hydro-

[1] This term is now a bad one, since synthetic camphor, identical with natural camphor, has now been prepared under several patents.

carbon recovered is not pinene, but camphene. The further action of hydrochloric acid on pinene results in the formation of dipentene dihydrochloride, showing that a molecular rearrangement has taken place. Pinene yields a characteristic compound with nitrosylchloride, $C_{10}H_{16}NOCl$, which is of great use in identifying the hydrocarbon. It is best prepared (*Ann. Chem.*, cclii., p. 251) by adding 15 c.c. of fuming hydrochloric acid to a well-cooled mixture of 50 c.c. each of turpentine, glacial acetic acid, and ethyl nitrite. The nitrosochloride separates as a crystalline precipitate, and can be washed with alcohol to purify it. It then melts at 103° and is optically inactive. By the action of alcoholic solutions of various amines on the nitrosochloride, characteristic nitrolamines are formed, of the general formula

$$C_{10}H_{16}\begin{matrix}NO\\NHR\end{matrix}$$

where R is the amine radicle. Of these pinene nitrol-piperidine melts at 118° and pinene nitrol-benzylamine at 122°. By treating pinene nitrosochloride with alcoholic potash nitrosopinene $C_{10}H_{15}NO$ is obtained. This body forms monoclinic crystals melting at 132°. The action of bromine on pinene gives rise to a solid di-bromide $C_{10}H_{16}Br_2$ melting at 169°, and possibly to a liquid tetrabromide.

The exact constitution of pinene is still a matter of doubt, but the most probable formula for this, and those for several of the other terpenes, are given below.

Camphene.—This is the only solid terpene known. It occurs to a small extent in a few essential oils, such as citronella, ginger and camphor oils. It occurs to a greater extent in the oil from *Pinus Siberica*, from which it can be separated in an impure condition. It is prepared artificially,

[1] Baeyer, however, holds that their constitution is $C_{10}H_{16}(NHR)N_2-O_2(RHN)C_{10}H_{16}$.

however, by several reactions, such, for example, as that mentioned above, *viz.*, the withdrawal of HCl from pinene monohydrochloride, or by the action of heat in the presence of acetic anhydride on bornylamine, $C_{10}H_{17}NH_2$, which causes the withdrawal of ammonia and leaves camphene, as follows:—

$$C_{10}H_{17}NH_2 = C_{10}H_{16} + NH_3.$$

It has been recognised in various oils by its ready conversion into isoborneol by the action of sulphuric and glacial acetic acids. It is present in small quantity in many oils in which pinene is found, but not in sufficient quantity to allow its isolation.

Camphene is a crystalline hydrocarbon, melting, according to Wallach, at 48° to 49° and boiling at 160° to 161°. Brühl, however, has found specimens made from pinene melting at 51° to 52°, and from bornyl chloride melting at 53·5° to 54°. The higher melting point is probably correct. The specific gravity of melted camphene is 0·850 at 48° according to Wallach and 0·8422 at 54° according to Brühl. Its refractive index is 1·4621.

The optical rotation of camphene is a matter of considerable uncertainty. It exists in the inactive as well as the *dextro-* and *laevo-*rotary varieties. Zelinski has isolated the terpene from Russian oil of turpentine, with a rotation of − 70° 45′, but as he could not obtain a nitrosochloride from it, it was probably impure. Bouchardat isolated a laevo-rotary specimen with $[a]_d = -80° 36'$, whilst Schindelmeiser isolated a specimen from *Pinus Siberica* with $[a]_d = -94° 30'$; but as this melted at 40°, the figure is of little value. Wallach finds − 85°, whilst the rotation of pure synthetic camphene is + 104°.

It is known in the inactive, as well as in the dextro- and laevo-rotary forms. The compounds of camphene are less stable than those of pinene, and have not, in many cases,

been prepared in a pure state. It is probable that natural camphene is a physical isomer of the synthetic body.

Limonene.—This terpene is one of the most important, as it forms from 80 to 90 per cent. of several essential oils. It is known in the dextro- and laevo-rotary forms, whilst when inactive it is known as dipentene, which will be discussed separately. This hydrocarbon has been described under the names hesperidene, citrene, carvene, etc. It occurs as dextro-limonene in oils of lemon, orange, bergamot, dill and other oils, and as laevo-limonene in certain pine needle oils, and Russian peppermint oil. It is a liquid of specific gravity 0·844 at 20°, boiling at 177° to 178°, of refractive index 1·4746. The purest samples of dextro- and laevo-limonene, isolated from essential oils, had for their optical activity – 105° and + 106·8° respectively (*Ann. Chem.*, cclii., p. 144). But pure dextro-limonene, prepared by reducing limonene tetrabromide resulting from the action of bromine on limonene from caraway oil, has a rotation + 125° 36′. With hydrochloric acid, limonene yields an optically active monohydrochloride, but in the presence of water dipentene dihydrochloride is formed. By the action of bromine, a tetrabromide $C_{10}H_{16}Br_4$ is formed, which melts at 104°, and is a very useful body for identifying the hydrocarbon. To prepare this compound, dissolve the isolated terpene fraction in four times its volume of glacial acetic acid, cool with ice water and gradually add bromine drop by drop until no more is absorbed. Crystals separate rapidly and should be filtered off with the aid of a pump, pressed on a porous plate and crystallised from an equal weight of warm acetic ether. A good yield is obtained, and the crystals should melt at 104°.

Both limonenes yield nitrosochlorides $C_{10}H_{16}NOCl$, each of which can be separated into two modifications. There are thus four limonene nitrosochlorides: they are known as the *a*- and *β*- varieties of the *dextro*- and *laevo*-rotary forms of

the terpenes. The *a*- and *β*- forms, however, yield the same carvoxime on treatment with alcoholic potash.

Here, as in every other case, the only difference between the derivatives of the two limonenes is that they are equally active optically in the opposite directions, and differ in the usual way in crystalline form. The nitrosochlorides, on boiling with alcoholic potash, yield nitroso-limonenes $C_{10}H_{15}NO$. These are identical with the two carvoximes, and their constitution is probably $C_{10}H_{14}.NOH$. They both melt at 72°. The carvoxime prepared from *dextro*-limonene-nitrosochloride is *laevo*-rotary, whilst that from *laevo*-limonene-nitrosochloride is *dextro*-rotary.

Tilden and Leech have prepared nitrosocyanides of limonene by the action of potassium cyanide on the nitroso-compounds. The following table gives the melting points and optical rotation of the principal of these and other limonene compounds.

Compounds.	Dextro- and Laevo- Melting Point.	Inactive Melting Point.	Dextro- Rotation.	Laevo- Rotation.
Limonene (pure) . .	—	—	+ 125·6°	—
Limonene (natural) .	—	—	+ 106·8°	- 105°
a-nitrosochloride . .	103-104°	—	+ 313·4°	- 314·8°
β-nitrosochloride . .	—	—	+ 240·8°	- 242·2°
a-nitrosocyanide . .	90-91°	81°	+ 152·7°	- 152·2°
Benzoyl-*a*-nitrosocyanide	108°	96°	+ 126·3°	- 127·2°
β-nitrosocyanide . .	140-141°	159-160°	- 31·6°	+ 30·6°
Benzoyl-*β*-nitrosocyanide	121°	98°	- 108·2°	+ 108·7°
a-amide	138°	155°	+ 174·9°	- 174°
Benzoyl-*a*-amide . .	152°	150°	+ 241·7°	- 242°
a-carbloxylic acid . .	97°	116°	+ 102·9°	- 103·9°
Dihydro-carvoxime . .	88·5°	115°	+ 9·46°	- 9·25°
Tetrabromide . . .	104°	125-126°	+ 73·3°	- 73·4°
Carvoxime . . .	72°	93°	- 39·3°	+ 39·7°
Monohydrochloride . .	—	—	- 40°	+ 39·5°
Nitrobenzylamine . .	92°	110°	+ 163·8°	- 163·6°

Dipentene.—This hydrocarbon was for some time regarded as a distinct individual, but it is now generally believed that,

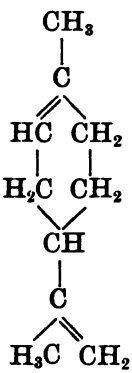
although it is such in a sense, it is the optically inactive form of limonene. On this hypothesis the limonenes bear to dipentene the same relationship as do the optically active tartaric acids to racemic acid. Dipentene occurs in several essential oils, for example, in camphor oil, in certain turpentine oils, in cubeb oil, and in thyme oil. It also results from the isomerisation of several other terpenes by means of heat. To obtain it in a state of purity, however, the best method is to boil dipentene dihydrochloride with an equal weight of dry sodium acetate and two parts of acetic acid for half an hour under a reflux condenser. The resulting oil is steam distilled, boiled with potash, and again distilled with steam and purified by fractional distillation.

It has often been stated that dipentene boils at a much higher temperature than limonene. This, however, is not so, and, doubtless, the examination of impure samples is responsible for this statement. Pure dipentene boils at about 178°, and has a specific gravity ·845 at 20°, and a refractive index 1·47308. The relationship of dipentene to limonene is here indicated, and is to a great extent proved by the fact that its derivatives can, without exception, be prepared by mixing equal quantities of the same derivatives of the two limonenes.

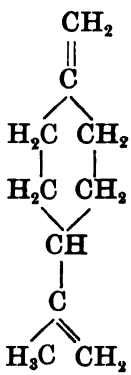
The following are amongst the most important of its derivatives. Dipentene dihydrochloride $C_{10}H_{16}.2HCl$ is formed by the action of gaseous hydrochloric acid on either dipentene, pinene or limonene. It forms crystals, melting at 50°, and boils at 118° to 120° under a pressure of 10 mm. The tetrabromide $C_{10}H_{16}Br_4$ is a useful body for identifying the terpene. It is prepared by the action of bromine on dipentene, and when pure melts at 125° to 126°. The nitrosochloride is quite analogous to the above-mentioned bodies. It occurs in two modifications. The action of alcoholic potash solution on this body gives the inactive nitroso-

dipentene, which is identical in every respect with inactive carvoxime, melting at 93°.

It is possible, however, that the view held by Semmler that dipentene is not identical with limonene is the correct one. He has suggested a nomenclature for the terpenes by which those compounds which contain a double linkage between the nucleus and the side chain should be called pseudo-compounds, whilst the compounds with the double linkage in the nucleus should be the ortho-compounds. He suggested the following formulæ:—



ortho-limonene



pseudo-limonene

Semmler then suggested that ortho-limonene might be ordinary limonene, and that dipentene had the pseudo formula, and that both these compounds would yield identical halogen derivatives with the breaking of the double linkage. He subsequently modified his view to some extent and considered that terpinene was represented by the pseudo-limonene formula. It is, however, quite possible that some such difference as this may account for the peculiar isomerism of these two terpenes.

Brühl gives the following figures for limonene:—

	Boiling Point (763 mm. press., corr.).	d.	a_D.	n_D.	$M_{D/2}$	$M_{D/2}$ calculated
d-limonene	175·5 to 176·5°	0·8402 at $\frac{21°}{4°}$	+104° 15′ at 19·5°	1·47428 at 21°	45·51	45·24
l-limonene	175·5 to 176·5°	0·8407 at $\frac{20·5°}{4°}$	−101° 30′ at 19·5°	1·47468 at 20·5°	45·52	45·24
d- and l-limonene in equal parts	175·5 to 176·5°	0·8409 at $\frac{20·7°}{4°}$	+1° 29′ at 19°	1·47448 at 20·7°	45·49	45·24
d- and so much l-limonene that the mixture was inactive	175·5 to 176·5°	0·8402 at $\frac{20·85°}{4°}$	± 0° at 20°	1·47443 at 20·85°	45·53	45·24

A most important piece of work has recently been achieved by W. H. Perkin Junior (*Chemical Society's Journal*, 1904, p. 654). He has succeeded in synthesising this important terpene in the following manner:—

Pentane-tri-carboxylic acid $CO_2H{\cdot}CH(CH_2 . CH_2 . COOH)_2$ is digested with acetic anhydride and then distilled, yielding a keto-hexahydro-benzoic acid. The esters of this acid readily react with magnesium-methyl-iodide, yielding, *inter alia*, *cis-delta*-hydroxy-hexahydro-para-toluic acid. This acid yields *delta*-bromohexahydrotoluic acid with fuming hydrobromic acid, and this again on treatment with sodium carbonate yields a tetra-hydro-para-toluic acid. Esters of this acid react with ethereal solution of magnesium-methyl-iodide, resulting in the formation of inactive terpineol. This in its turn, with potassium bisulphate, yields inactive dipentene. This body boils at 181° to 182°, and yields a tetrabromide melting at 125°, and a dihydrochloride melting at 48° to 50°. The investigator is still working on the subject.

Fenchene.—This terpene is not found in nature, or if so, only to a very minute extent. It may be prepared by reducing the ketone, fenchone $C_{10}H_{16}O$ to its alcohol fenchyl

alcohol, $C_{10}H_{17}OH$, from which the elements of water can be separated by means of potassium bisulphate at a high temperature, when fenchene $C_{10}H_{16}$ results. It is, however, certain that the terpene so obtained is a mixture of probably two chemical and several stereo-chemical isomers. The chemistry of this terpene is in an unsatisfactory state, as it is doubtful as to whether any pure individual has been isolated. According to Wallach fenchene is a liquid boiling at 155° to 156°, of specific gravity 0·867 and refractive index 1·4690 at 20°. According to Gardner and Cockburn its boiling point is 150° to 152°, its specific gravity 0·8667 at 18° and its optical rotation − 6·46°. Wallach has, later, found that when *l*-fenchyl alcohol prepared from *d*-fenchone is treated as above, it yields two fenchyl chlorides, and these in turn yield two fenchenes, one *laevo*- and the other *dextro*-rotary. They are both derived from dextro-fenchene and Wallach designated them *d-dextro*-fenchene and *d-laevo*-fenchone.

A laevo-fenchene also appears to exist, and Wallach gives + 21° and − 21° as the limits of optical rotation. Kondakoff also describes two isomeric fenchenes, of which one was isolated pure, by the action of alcoholic potash on fenchyl bromide. This has a specific gravity 0·8385 at 20° and a rotatory power of − 55°. The most modern researches are those of Semmler and Kondakoff, the latter of whose results point to the formation of two isomeric semi-cyclic terpenes, which he would call "camphor fenchene" and "isofenchone fenchene". Semmler, however, does not agree with this. The matter is thus seen to be in a somewhat chaotic condition. Fenchene combines with two atoms of bromine, yielding a liquid dibromide, which has not yet been obtained in a pure state. Fenchene is a stable terpene, resisting the action of nitric acid in the cold to a much greater extent than other terpenes.

Sylvestrene.—This terpene occurs in Swedish and Russian oils of turpentine and various pine oils. It can be prepared,

according to Wallach (*Ann. Chem.*, ccxxxix., p. 24), by diluting with an equal volume of ether the fraction of Swedish turpentine which boils between 174° and 178°. This is saturated with dry hydrochloric acid gas, and, after allowing the whole to stand for two days, the ether is distilled off, and the residue crystallised. By recrystallisation from warm alcohol it can be obtained pure, when it melts at 72°. The hydrocarbon is obtained from its dihydrochloride by heating with aniline, or with acetic acid and sodium acetate. Sylvestrene has an odour recalling that of bergamot. It boils at 176° to 177°, has a specific gravity ·851 at 15·5°, and a refractive index 1·4747. Natural sylvestrene is dextro-rotary $[\alpha]_d = + 66·3°$. A characteristic colour reaction of this terpene is as follows: one drop of sylvestrene is dissolved in a little acetic anhydride, and one drop of concentrated sulphuric acid is added. An intense blue colour results. It is a most stable terpene, which polymerises under the influence of heat, without yielding any of the isomeric terpenes. It forms a characteristic dihydrochloride, already mentioned, and a tetrabromide $C_{10}H_{16}Br_4$, melting at 135°. The nitrosochloride melts at 106° to 107°. The various compounds of sylvestrene which have been prepared are, as is the hydrocarbon, dextro-rotary.

Carvestrene.—This hydrocarbon is, in all probability, the optically inactive variety of sylvestrene. But this cannot be definitely proved until it is resolved into the two optically active varieties, or until laevo-sylvestrene is discovered, when a mixture of the two sylvestrenes should yield carvestrene. It yields the characteristic sylvestrene colour reaction mentioned above, which the other terpenes do not. Carvestrene has not been found in nature, having been prepared by Baeyer (*Berichte*, xxvii., p. 3485) by the distillation of carylamine hydrochloride, $C_{10}H_{17}NH_2 . HCl$, in an atmosphere of dry hydrochloric acid gas. It is an optically inactive

liquid, boiling at 178°. It forms a crystalline dihydrochloride, $C_{10}H_{16}2HCl$, melting at 52·5°, and a dihydrobromide melting at 49°.

Perkin and Tattersal have achieved a complete synthesis of carvestrene identical in all respects with Baeyer's hydrocarbon, starting from *m*-hydroxy-benzoic acid (*Chem. Soc. Journal*, 1907, 480). This synthesis establishes the formula

$$CH\begin{matrix}\diagup C(CH_3)\,.\,CH \\ \diagdown CH_2-CH_2\end{matrix}\diagup CH\,.\,C(CH_3)\,.\,CH_2.$$

Phellandrene.—In the previous edition of this work phellandrene was described as a single terpene. Much confusion has been introduced into the chemistry of the terpenes by the use of the qualifications *a* and *β* to distinguish bodies at one time believed to be identical, but later shown to be different. This is to be regretted, as it is obviously the proper course to give a new name to one of the bodies, leaving the old name for the other.

The old "phellandrene" was isolated from oils of certain species of eucalyptus, elemi, bitter fennel and water fennel, and was described as a terpene of specific gravity 0·8558 at 10°, and an optical rotation of ± 18°.

Wallach has, however, now shown that the dextro-phellandrene from elemi oil and that from bitter fennel oil are identical, and that laevo-phellandrene from eucalyptus oil is its optical antipode, and to these bodies he assigns the name *d*-*a*-phellandrene and *l*-*a*-phellandrene. The dextro-phellandrene from water fennel oil is a different body and he terms this *d*-*β*-phellandrene. The optical antipode of this is not yet discovered. All varieties of phellandrene are unstable and easily susceptible of change. They readily yield a nitrite, $C_{10}H_{16}N_2O_2$, which is prepared in the following manner. Five grammes of sodium nitrite in 8 c.c. of water are added to 5 c.c. of the fraction of an oil rich in phellandrene, dissolved in

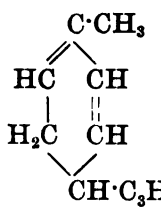
10 c.c. of petroleum ether, and the mixture well shaken; 5 c.c. of acetic acid are then added. The resulting crystals are washed with water and alcohol, and then dissolved in chloroform, from which the pure compound is precipitated by the addition of alcohol. The following figures are the most authentic for the phellandrenes:—

	Specific Gravity.	*Rotation.*	*Refractive Index.*
Dextro-α-phellandrene . .	0·846		1·4782
Dextro-β-phellandrene . .	0·848	+ 14°45′	1·4759

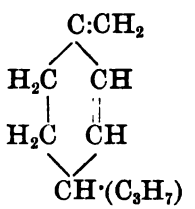
Each variety of phellandrene yields two isomeric nitrites, six of which have been prepared and have the following characters:—

	Specific Rotation.	*Melting Point.*
Dextro-α-phellandrene α-nitrite .	− 138·4°	112°-113°
Laevo-α-phellandrene α-nitrite . .	+ 135·9°	112°-113°
Dextro-α-phellandrene β-nitrite .	+ 45·9°	105°
Laevo-α-phellandrene β-nitrite . .	− 40·8°	105°
Dextro-β-phellandrene α-nitrite .	− 159·3°	102°
Dextro-β-phellandrene β-nitrite .	+ 0°	97°-98°

The other two varieties have not yet been prepared. A long study of the conversion products of phellandrene nitrite leads Wallach to consider the following to be the correct formulæ for α-phellandrene and β-phellandrene:—



α-phellandrene



β-phellandrene

Terpinolene.—This terpene has not been found in nature. It is formed by the isomerisation of other terpenes by the action of sulphuric acid, or by heating cineol or terpineol

with sulphuric or phosphoric acid. It is known only in the optically inactive variety. It boils at about 185°, and has a specific gravity of about ·855. It forms a well-defined dibromide melting at 69°, and a tetrabromide melting at 116°.

Terpinene.—This terpene was found by Weber in oil of cardamoms (*Ann. Chem.*, ccxxxviii., p. 107). It results, like terpinolene, from the isomerisation of several of the other terpenes by the action of sulphuric acid. It boils at about 180°, and has a specific gravity ·847 at 20°, and a refractive index 1·48458. It is optically inactive. It forms a nitrosite $C_{10}H_{16}N_2O_3$ melting at 155°. The halogen addition products are liquid. The dihydrochloride melts at 52°.

Thujene.—This terpene has not been isolated from any essential oil. Tschugaeff has prepared a terpene, apparently a bicyclic hydrocarbon, by the dry distillation of thujyl xanthogenate. It is a mobile liquid of delicate odour, recalling those of thuja and pine oils, boiling at 151° to 153°, of specific gravity 0·8275 at 20° C., and of refractive index 1·45042. It is slightly laevo-rotary. It is very unstable and on account of its low specific gravity may be classed half-way between the ordinary and the olefinic terpenes. The terpene prepared by the distillation of thujylamine hydrochloride, which was formerly known as thujene, and which is identical with Semmler's tanacetene, is now better termed iso-thujene. This body is described by Semmler as of specific gravity 0·8508, and refractive index 1·4760. Wallach, however, describes it as of specific gravity 0·836 and refractive index 1·47145. This terpene is of little importance practically.

The following table summarises the published figures for this troublesome hydrocarbon:—

Boiling Point.	Specific Gravity.	Rotation.	Refractive Index.
Semmler's Thujene—			
60°-68° (14 mm.)	0·8508 at 15°		1·47600
Wallach's Thujene—			
170°-172° (760 mm.)	0·8360 at 15°		1·47145
Tschugaeff's Thujene—			
151°-152·5° „	0·8275 at 15°		1·45042
Kondakoff's Hydrocarbon—			
1. 147°-150°	0·8258 at 18°	+ 48° 32′	1·44929
2. 150°-151·5°	0·8260 at 18°	+ 40° 15′	1·45001
3. 151·5°-152·5°	0·8279 at 17°	+ 28° 12′	1·44999
4. 152·5°-156°	0·8286 at 17°	+ 12° 1′	1·44909
5. 156°-168°	0·8286 at 17°	+ 8° 33′	1·45259

An examination of these figures, especially the specific gravities and refractive indices, would certainly lead one to suppose that Tschugaeff's "thujene" contains aliphatic hydrocarbons.

Sabinene.—This terpene was discovered in oil of savin by Semmler. It belongs to what that chemist has called the *pseudo*-series (*Berichte*, 1900, 1455). It is a liquid of specific gravity 0·840, refractive index 1·4660 at 20° and boils at 162° to 166°. It is transformed into terpinene by boiling with dilute sulphuric acid, and yields sabinenic acid $C_{10}H_{16}O_3$ on oxidation with permanganic acid. It forms a monohydrochloride boiling at 87° to 92° at 12 mm., and of specific gravity 0·970 and refractive index 1·4824. This terpene is bicyclic, and is also found in *Pilea* oil.

Firpene.—Frankforter and Frany have isolated a terpene, which they term firpene from the American oleoresin known as "Western Fir" turpentine. It differs in odour and in properties from pinene, which it somewhat resembles. It has the following characters: specific gravity at 20° = 0·8598; boiling point, 152° to 154°; refractive index, 1·47299 at 20°; optical rotation − 47·2°. It yields a hydrochloride melting at 130° to 131°. It yields a dihydrochloride, and a hydrobromide melting at 102°. It does not yield a crystalline nitrosylchloride.

SESQUITERPENES.

The sesquiterpenes are polymers of the terpenes, with which they are closely related, of the formula $C_{15}H_{24}$. A large number no doubt exist, but on account of the difficulty in purifying the hydrocarbons none can be said to be established as definite individuals until pure derivatives are prepared, whose properties can be studied. The principal well-defined sesquiterpenes appear to be the following: *cadinene, caryophyllene, cedrene, clovene, humulene, ledene, patchoulene, atractylene, santalene* and *zingiberene*, and a hydrocarbon occurring in the oil of *Cannabis indica*.

Cadinene.—This sesquiterpene is found in its laevo-rotary form in the oils of cade, patchouli, galbanum and others. Dextro-cadinene is found in the so-called West Indian santal oil. To prepare it in the pure state, Wallach recommends the following process. The fraction of oil of cade boiling between 260° and 280° is saturated with hydrochloric acid gas, and the resulting cadinene hydrochloride is purified and reconverted into the hydrocarbon by heating it with aniline. When pure, cadinene boils at 275°, and has a specific gravity ·921 at 15·5°, and a refractive index 1·5065. Its laevo-rotation is $[\alpha]_d = -98{\cdot}6°$. Dextro-cadinene is found in the oil of *Cedrus Atlantica*. It forms a dihydrochloride, melting at 117° to 118°, of the formula $C_{15}H_{24}2HCl$, and corresponding compounds with hydrobromic and hydriodic acids. All these compounds are laevo-rotary. The dextro-variety yields corresponding dextro-rotary compounds.

Cadinene yields a well-defined nitrosate when one part of cadinene is cooled in a freezing mixture, and dissolved in three parts of acetic acid. To this is added one part of ethyl nitrite. A mixture of equal parts of concentrated nitric acid and glacial acetic acid is now slowly added, and the whole is

diluted with alcohol. The resulting precipitate is filtered with the aid of a pump and washed with alcohol. Cadinene nitrosate is a white crystalline powder melting at 105° to 110° with decomposition.

Cadinene yields a beautiful colour reaction when a few drops are dissolved in chloroform and shaken with a few drops of concentrated sulphuric acid. The liquid turns dark green, passing to blue and becoming red on warming. If acetic acid be used instead of sulphuric acid, the blue colour is more marked.

Caryophyllene.—It is doubtful whether this body has yet been prepared in a state of absolute purity. It was first characterised as a definite sesquiterpene by Wallach, who converted it into a crystalline alcohol, caryophyllene alcohol. The purest caryophyllene obtained from clove oil, in which it occurs to a considerable extent, had the following characteristics: boiling point, 259°; specific gravity at 15°, 0·9030; refractive index, 1·4998. Its rotation was −9°.

Caryophyllene yields a hydrochloride melting at 67° to 70° by saturating its ethereal solution with dry hydrochloric acid gas and allowing it to stand for a long time with alcohol. The nitrosate $C_{15}H_{24}N_2O_4$ is prepared by mixing equal amounts of caryophyllene, acetic acid and ethyl nitrite in a freezing mixture, and adding the same amounts of nitric and acetic acids mixed. After well shaking, alcohol is added, when the nitrosate is precipitated, and melts at 148° to 149°. A nitrosite $C_{15}H_{24}N_2O_3$ is prepared by mixing 25 c.c. of caryophyllene, 25 c.c. of petroleum ether and 25 c.c. of saturated solution of sodium nitrite. Acetic acid is then slowly added and the whole well shaken. The whole is frozen for two hours, when the nitrosite separates as a solid mass of blue needles melting at 113°. The specific rotary power of this compound is + 103°. A nitrosochloride $(C_{15}H_{24}NOCl)_2$ can be prepared by the action of alcoholic hydrochloric acid on a mixture of caryophyllene,

alcohol, ethyl acetate and ethyl nitrite in a freezing mixture. It melts with decomposition at 158° to 162°. Deussen has shown, however, that this body is a mixture of two isomeric nitrosochlorides, melting at 159° and 179° respectively (*Annalen*, 1907, 356, i.). To prepare the crystalline alcohol, 25 grammes of crude caryophyllene (obtained from oil of cloves by distillation, or by absorbing the eugenol with solution of caustic alkali) are added to a mixture of 1000 grammes of acetic acid, 20 grammes of concentrated sulphuric acid, and 40 grammes of water. This is heated for several hours in the water bath. The product of the reaction is distilled with steam, when, during the latter part of the process, the solid alcohol distils over. This is separated and dried, and finally re-distilled. The alcohol, $C_{15}H_{25}OH$, boils at 288°, and sublimes in needles, melting at 95°. It is almost insoluble in water, but soluble in the usual organic liquids. It is optically inactive. It is characterised by the formation of a phenylurethane, $C_{15}H_{25}O \cdot CO \cdot NH \cdot C_6H_5$, melting at 136°. It also forms an acetate, $C_{15}H_{25}O \cdot COCH_3$.

Cedrene is the characteristic sesquiterpene of cedar wood oil. Its properties are, however, not yet definitely agreed upon, as it is doubtful whether it has been prepared in a pure state. According to Rousset (*Bull. Soc. Chim.*, 1897, p. 485) its optical activity is − 47·9°, whilst other chemists give it as − 60°. Its specific gravity is about ·936 and boiling point 262°. Its refractive index is 1·50233 at 20°. Chapoteaut has alleged that the hydrocarbon of cedar wood oil has the formula $C_{15}H_{22}$, and that it is identical with that yielded by the action of phosphoric anhydride on santalal, one of the constituents of santal wood oil, but this is not probable.

Cedar "camphor," or cedrol, a crystalline constituent of cedar wood oil, is probably the sesquiterpene alcohol corresponding to cedrene. Its composition is $C_{15}H_{25}OH$, and when dehydrated with phosphoric anhydride it yields a terpene,

which Walter believed to be cedrene. Schimmel & Co. have dehydrated cedrol by means of formic acid, and find the resulting terpene to boil at 262° to 263°, and to have a rotation of − 80°. It is probable that this is pure cedrene, and that the lower rotations observed are due to the terpene not having been separated from the oil in a pure condition.

Clovene.—This hydrocarbon has not been found in nature. When caryophyllene alcohol is treated with dehydrating agents, it yields up water, with the formation of a hydrocarbon which is not identical with caryophyllene. This is termed clovene. Its boiling point is nearly identical with that of caryophyllene, *viz.*, 262°, but its specific gravity is ·930 at 18°. Its refractive index is 1·5006. It is further distinguished from the hydrocarbon to which it owes its existence, by not yielding a crystalline alcohol, when treated in the way described for obtaining caryophyllene alcohol from caryophyllene.

Humulene.—This hydrocarbon was discovered in oil of hops by Chapman (*Jour. Chem. Soc.*, 1895, p. 54). It is a liquid boiling at 265°, under ordinary pressure, and of specific gravity ·9001. It forms liquid halogen compounds, and does not yield a crystalline alcohol. The nitrosochloride, however, $C_{15}H_{24}NOCl$, is crystalline, and melts at 164°. The nitrosate, $C_{15}H_{24}N_2O_4$, melts at 162°.

Ledene.—This sesquiterpene has not been found naturally, it having been prepared by dehydrating ledum camphor $C_{15}H_{26}O$ (from *Ledum palustre*). It boils at 255°, but its properties are not well understood.

Patchoulene.—This, too, is obtained by dehydrating its corresponding alcohol, the so-called patchouli camphor $C_{15}H_{26}O$. It boils at 254°, has a specific gravity ·939 at 23°, and a refractive index 1·50094. It closely resembles cedar in odour.

Atractylene.—Gadamer and Amenomiya (*Archiv der*

Pharmazie, 1903, 22) have prepared a well-defined terpene, which they term atractylene, by dehydrating atractylol, a crystalline sesquiterpene alcohol separated from the oil of *Atractylis ovata*. It is an oil with an odour of cedar wood, boiling at 125° to 126° at 10 mm., of specific gravity 0·9101 at 20° and refractive index 1·50893. It polymerises on keeping.

Santalene.—Von Soden and Müller first observed the presence of a sesquiterpene in oil of santal wood. They described it as of specific gravity 0·898, boiling point 261° and optical rotation − 21°. No crystalline compounds could be prepared. Guerbet (*Bull. Soc. Chim.*, 1900, 540) states that two sesquiterpenes are present in the oil, to which he assigns the names *α*-santalene and *β*-santalene. The properties of these two sesquiterpenes are as follows:—

	Boiling Point.	*Specific Gravity at 0°.*	*Rotation.*
α-Santalene	253°-254°	0·9134	− 13·98°
β-Santalene	263°-264°	0·9139	− 28·55°

Both hydrocarbons form acetates when heated with glacial acetic acid in sealed tubes. *α*-santalene forms a liquid dihydrochloride of optical rotation + 6°, when dry hydrochloric acid is passed through its ethereal solution. It also forms a crystalline nitrosochloride melting with decomposition at 122°, and a nitrol-piperidide melting at 108° to 109°. *β*-santalene forms corresponding compounds, the dihydrochloride having a rotary power + 8°. It forms, however, two isomeric nitrosochlorides, $C_{15}H_{24}NOCl$. They may be separated by fractional crystallisation from alcohol. One melts at 106°, the other at 152°. The corresponding nitrol-piperidides melt at 105° and 101° respectively. It may here be mentioned that the body termed amyrol, obtained from the so-called West Indian santal oil, and originally known as santalol, yields a sesquiterpene on dehydration.

Zingiberene.—This sesquiterpene forms the chief constituent of oil of ginger. It is obtained in a nearly pure condition by the repeated fractionation of the oil under reduced pressure. It boils at 160° to 161° at 32 mm., and at 269° to 270° at 760 mm. It has the specific gravity 0·8731 at 20°, refractive index 1·49399 at 20°, and optical rotation about − 70°. Its dihydrochloride, $C_{15}H_{24}2HCl$, melts at 168° to 169°; the nitrosochloride, $C_{15}H_{24}NOCl$, melts at 96° to 97°, the nitrosite, $C_{15}H_{24}N_2O_3$, at 97° to 98°, and the nitrosate, $C_{15}H_{24}N_2O_4$, at 86° to 88°.

Sesquiterpene from Oil of Cannabis Indica.—This may fairly be considered a definite body, as it has been isolated by many different observers and described by them at different times. Valenta (*Gazzetta*, 1880, p. 540) first mentions it. Vignolo (*Gazzetta*, 1895, p. 110) describes it as a mobile liquid boiling at 256°, of specific gravity ·897 at 15°, and slightly laevo-rotary. Wood, Spivey and Easterfield (*Jour. Chem. Soc.*, 1896, p. 543) give the boiling point as 258° to 259°, the specific gravity as ·898 at 18°, and the rotation as − 8·6°. The name *cannibene* may be applied to this hydrocarbon. Personne first gave this name to what is now known to be an impure compound obtained from the oil.

Olefinic Terpenes and Sesquiterpenes.

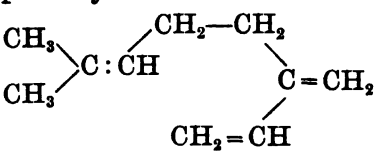
There are several so-called terpenes and sesquiterpenes, usually described as olefinic, and which are not true terpenes at all, belonging, as they do, to the open-chain series of compounds. Their general relation to the terpenes and to essential oils generally renders it convenient, however, that they should be briefly described here. The first member of this group to be described was the artificially prepared anhydrogeraniol discovered by Semmler. Although it is probable that the oils of hops and of origanum (Smyrna) contain such bodies, the only well-defined, naturally occurring olefinic terpenes are myrcene and ocimene. The author has also found

Compound.	Boiling Point.	Sp. Gr. at 15·5°.	Optical Rotation	Ref Index at 20°.	Hydrochloride Melting Point.		Bromide Melting Point.		Nitrosochloride		Nitroso-compound.		Nitrite		Remarks.
					Mono-	Di-	Di-	Tetra-	Melting Point.	Rotation.	Melting Point.	Rotation.	Melting Point.	Rotation.	
Pinene	155°-156°	·861	± 40°	1·4655	125°	—	169	—	103°	0°	132°	0°	—	—	
Camphene	160°	·850 (at 50°)	± 85°	1·4621	—	—	—	—	—	—	—	—	—	—	
Limonene	177°-178°	·848	± 125°	1·4746	—	—	—	104°	103°	± 314°	72°	± 39·5°	—	—	Figures for nitrosochloride are for the α variety. Rotations of the nitroso-compounds are of opposite sign to those of the terpenes (*vide* limonene).
Dipentene	178°	·848	0°	1·4740	—	50°	—	125°	103°	0°	93°	0°	—	—	Highest rotation of natural limonene obtained is 106°.
Fenchene	156°	·864	0°	1·4690	—	—	—	—	—	—	—	—	—	—	
Sylvestrene	176°	·851	+ 66·3°	1·4747	—	72°	—	135°	106°	—	—	—	—	—	
Carvestrene	178°	—	0°	—	—	52·5°	—	—	—	—	—	—	—	—	
Phellandrene (α)	170°	·846	—	1·4732	—	—	—	—	—	—	—	—	—	—	Rotation of nitrite is of opposite sign to the terpene (*vide* under phellandrene).
„ (β)	170°	·848	+ 14·5°	1·4759	—	—	—	—	—	—	—	—	—	—	
Terpinolene	185°-190°	·855	0°	—	—	—	69°	116°	—	—	—	—	—	—	
Terpinene	180°	·849	0°	1·4846	—	52°	—	—	—	—	—	—	155°*	—	* Nitrosite.
Thujene	151°	·851	—	1·4760	—	—	—	—	—	—	—	—	—	—	
Sabinene	162°-166°	·840	—	1·4660	—	—	—	—	—	—	—	—	—	—	
Cadinene	275°	·921	- 98·6°	1·5068	—	117°	—	—	—	—	—	—	—	—	
Caryophyllene	259°	·903	9°	1·4998	67°	—	—	—	162°	—	—	—	148°*	—	* Nitrosate $C_{15}H_{24}N_2O_4$. Yields a solid alcohol melting at 95°, $C_{15}H_{25}OH$.
Clovene	262°	·932	0°	1·5003	—	—	—	—	—	—	—	—	—	—	
Cedrene	261°	·936	- 80°	—	—	—	—	—	—	—	—	—	—	—	
Humulene	265°	·900	- ·5°	—	—	—	—	—	164°	—	—	—	162°*	—	* Nitrosate.
Ledene	255°	—	—	—	—	—	—	—	—	—	—	—	—	—	
Patchoulene	254°	·945	—	—	—	—	—	—	—	—	—	—	—	—	
Cannibene (?)	258°	·897	- 9°	—	—	—	—	—	—	—	—	—	—	—	
Atractylene	—	·9130	—	1·5089	—	—	—	—	—	—	—	—	—	—	
Santalene (α)	254°	·9034	- 14°	—	—	—	—	—	122°	—	—	—	—	—	
„ (β)	264°	·9099	- 28·5°	—	—	—	—	—	106° 152°	—	—	—	—	—	
Zingiberene	270°	·876	- 70°	1·49399	—	—	—	—	96-97°	—	—	—	—	—	

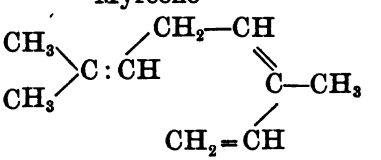
a similar body in West Indian lemon-grass oil, but it is not yet fully investigated.

Myrcene.—This body is found in oils of bay and sassafras leaves. It has a characteristically low specific gravity, 0·801 at 15°, and a refractive index of 1·4700 (Enklaar, *Thesis*, Utrecht, 1905). It boils at 67° to 68° at 20 mm. pressure. Myrcene rapidly oxidises and resinifies by exposure to the air.

Ocimene.—This compound is found in the leaves of *Ocimum basilicum.* Its characters are very similar to those of myrcene: it boils at 172°, specific gravity, 0·8031, and refractive index at 20°, 1·4857. It does not, however, alter to any considerable extent by exposure to the atmosphere. But on heating it is converted into an isomer, allo-ocimene, which boils at 188°; has a specific gravity, 0·8172 at 15·5°, and a refractive index, 1·5296. The constitutions of these two bodies are probably:—



Myrcene



Ocimene

Amongst the olefinic sesquiterpenes, bodies which appear to bear the same relation to the sesquiterpenes proper, as the olefinic terpenes do to the terpenes, only a few have been well characterised.

From Citronella Oil.—Schimmel & Co. have isolated a body of this nature from citronella oil. It has the following characters: specific gravity, 0·8643 at 15°; refractive index at

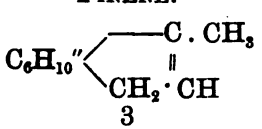
15°, 1·5185; optical rotation, + 1° 28′; boiling point, 270° to 280° with decomposition, or 157° at 15 mm.

Limene.—This compound was isolated from the distilled oil of limes by Burgess, and also occurs in the oil of *Piper volkensii*. According to its discoverer it has the following characters: specific gravity at 15°, 0·873; refractive index at 15°, 1·4935; boiling point, 131° at 9 mm., or 262° at 750° with slight decomposition. It is optically inactive.

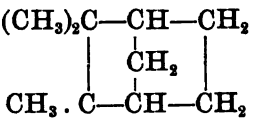
There have been numerous other sesquiterpenes described, but they have always been prepared in a doubtful state of purity. But little information is given of their properties, and less of their derivatives. There is no doubt that a closer examination of these will establish the chemical individuality of some, but will prove that many are but impure forms of bodies already known and described. An extensive and systematic study of this complex group of bodies is very urgently needed. The foregoing table (p. 31) summarises the chief physical characters of the well-known terpenes and sesquiterpenes. Some of them are necessarily only approximate.

The following diagrammatic formulæ are amongst the most probable of those which have been put forward as representing the constitution of pinene, camphene and limonene. Two remarks, however, must be made in this connection. The instability of this group of bodies, and the ease with which they enter into reaction, are such as to have so far prevented their constitution being settled at all definitely. Secondly, so many different views are held on the matter, that those formulæ only which appear to the author to have most experimental work in their favour have been selected.

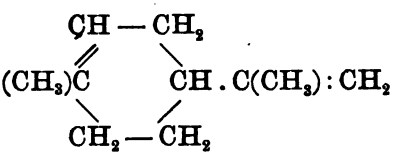
PINENE.



CAMPHENE.



LIMONENE AND DIPENTENE.



II. THE CAMPHOR SERIES.

Under this heading may be classed a number of oxygenated compounds which are closely related in their chemical constitution to the terpenes. The more important of these may be grouped in pairs—an alcohol with its corresponding ketone. A few other bodies than these will be described here, chiefly as a matter of convenience. The following, then, are the most important, and better known of these bodies:—

Alcohols.		*Ketones.*	
Borneol,	$C_{10}H_{17}OH$	Camphor,	$C_{10}H_{16}O$.
Isoborneol,	$C_{10}H_{17}OH$	—	
Fenchyl alcohol,	$C_{10}H_{17}OH$	Fenchone,	$C_{10}H_{16}O$.
Thujyl alcohol,	$C_{10}H_{17}OH$	Thujone,	$C_{10}H_{16}O$.
Terpineol,	$C_{10}H_{17}OH$	—	
Pulegol,	$C_{10}H_{17}OH$	Pulegone,	$C_{10}H_{16}O$.
Menthol,	$C_{10}H_{19}OH$	Menthone,	$C_{10}H_{18}O$.

Borneol, $C_{10}H_{17}OH$.—This compound occurs naturally, in both optically active modifications; as dextro-borneol in the wood of *Dryobalanops camphora* (Borneo camphor), and as laevo-borneol in *Blumea balsamifera* (Ngai camphor). It also occurs optically inactive. It forms crystalline masses, or, when recrystallised from petroleum ether, fine tablets which, when quite pure, melt at 203°. Its boiling point is only a few degrees higher, *viz.*, 212°. According to Bouchardat the melting point is lower than that given, but this is un-

doubtedly due to the fact that his borneol was impure, probably containing some isoborneol. Borneol can be prepared artificially by reducing its ketone (camphor) with sodium. Fifty grammes of pure camphor are dissolved in 500 c.c. of nearly absolute alcohol, and treated with 60 grammes of sodium. After the reaction is complete the whole is poured into a large volume of water, and the resulting borneol is collected, washed, pressed and recrystallised from petroleum ether. This method of preparation, however, yields a mixture of borneol and isoborneol. The chemically pure body is best prepared by the saponification of its acetate. On oxidation, the converse reaction takes place, with the formation of camphor. Borneol forms a series of esters with the organic acids, of which bornyl acetate is most frequently found in nature. This body melts at 29°, and has a specific gravity of ·991 at 15°. It is optically active. In common with a large number of alcoholic bodies borneol forms a crystalline phenylurethane. This can be prepared by the interaction of phenylisocyanate and borneol. It melts at 138°. Bornyl chloride, prepared by the action of phosphorus pentachloride on borneol, melts at 157°.

Borneol forms crystalline compounds with chloral and bromal, the former melting at 55° and the latter at 98°.

The remarks made under camphor as to its probable constitution apply to borneol, remembering that the two bodies are related to one another as an alcohol and ketone.

Bertram and Walbaum give the following as the characters of several of the borneol esters :—

	Boiling Point at 10 mm.	Optical Rotation.	Specific Gravity.	Refractive Index at 15°.
Formate .	90°	+ 31°	1·013	1·47078
Acetate .	98°	− 38° 20′	0·991	1·46635
Propionate	110°	+ 24°	0·978	1·46435
Butyrate .	121°	+ 22°	0·966	1·46380
Valerianate	128°-130°	+ 20°	0·956	1·46280

Bredt considers borneol and isoborneol (*q.v.*) as stereo-isomers, the OH group being turned away from the ring in borneol and less capable of reaction than the corresponding group in isoborneol, which is turned towards the centre of the ring. On this hypothesis he calls borneol "exoborneol" and isoborneol "endoborneol".

Isoborneol.—This alcohol is isomeric with borneol, which it closely resembles. In the opinion of Jünger, the two bodies are geometrical isomerides of otherwise identical chemical structure, which, as mentioned above, is a view shared by Bredt. Isoborneol is obtained together with borneol, when camphor is reduced with sodium, and also by hydrating the terpene, camphene, by means of acetic and sulphuric acid (*Jour. prakt. Chem.*, xlix., p. 1). When isoborneol is heated with zinc chloride it yields camphene, whereas borneol, under the same treatment, remains unaltered. The compounds of isoborneol are analogous in every respect to those of borneol. The following table, compiled from Heusler's *Die Terpene*, gives a comparison of some of their properties:—

	Borneol.	*Isoborneol.*
Melting point	208° . .	212°.
Boiling point	212° . .	Undetermined.
Specific rotation (approximate)	35° . .	4°.
Phenylurethane . . .	Melts at 138°	Melts at 138°.
Chloral compound . . .	Melts at 55°	Liquid.
Acetic ester	Melts at 29°	Liquid.
Behaviour with zinc chloride	Unaltered .	Yields camphene.

Camphor, $C_{10}H_{16}O$.—This body occurs in the wood of the camphor tree (*Laurus camphora*) as dextro-camphor. This is the ordinary camphor of commerce, known as Japan camphor, whilst the less common laevo-camphor is found in the oil of *Matricaria parthenium*. Camphor can also be obtained by the oxidation of borneol or isoborneol with nitric acid. Camphor may be prepared from turpentine in

numerous ways, and there are many patents existing for its artificial preparation. Those interested in several of these patents state that they have every reason to believe that artificial camphor is on the eve of being a commercial success. Amongst the methods may be enumerated the following:—

(1) Esters of borneol are obtained by the action of dry oxalic acid on turpentine under suitable conditions. From these borneol is obtained by saponification and is oxidised to camphor. Some other acids produce a similar result, as for example salicylic and chlorobenzoic acids.

(2) Pinene hydrochloride is prepared in the usual manner from turpentine, and this is allowed to react with acetate of silver. Isobornyl acetate is formed, which is hydrolysed, and the isoborneol oxidised to camphor. Acetate of lead is also used, as is also acetate of zinc.

(3) The action of magnesium on pinene hydrochloride gives rise to bornyl esters, and camphor can be obtained from these in the usual manner.

(4) Pinene hydrochloride is treated by one of the reagents which abstract HCl, and so converted into camphene (*q.v.*). This is heated with acetic and sulphuric acids and so converted into isobornyl acetate. Camphor results in the usual manner.

It forms a colourless, translucent mass, which crystallises well from alcohol; it is easily sublimable at low temperatures. It melts at 175°, boils at 204°, and has a specific rotation of ± 44°. Inactive camphor, formed by the mixture of equal quantities of the oppositely active isomers, or by the oxidation of inactive borneol, melts at 179°. Camphor is the ketone of the alcohol borneol, and forms a number of well-characterised crystalline derivatives. Amongst these are the semicarbazone, the phenylhydrazide, and the oxime, all characteristic of bodies containing the . CO. group. The semicarbazone, $C_{10}H_{16}: N_2H . CO . NH_2$, melts at 236° to 238°. The hydrazide, $C_{10}H_{16}: N_2HC_6H_5$, results from the action of

phenylhydrazine. The oxime, $C_{10}H_{16}.NOH$, is prepared by the action of hydroxylamine on camphor. It melts at 118°, and when reduced by means of sodium, yields the base bornylamine $C_{10}H_{17}NH_2$.

When distilled with phosphorus pentoxide, camphor yields cymene, and with iodine, carvacrol. Both of these bodies are *para*-derivatives of benzene. On oxidation with nitric acid, camphor yields many acids, of which the chief are camphoric acid $C_{10}H_{16}O_4$, camphanic acid $C_{10}H_{14}O_4$, and camphoronic acid $C_9H_{14}O_6$. The constitution of these acids has an important bearing on that of camphor. Many formulæ have been suggested for camphor during the past few years, but that of Bredt is now universally accepted, and has received complete confirmation by Komppa's synthesis of camphoric acid. This synthesis is fully described in the *Berichte*, 36, 4332, and confirms the formula for camphoric acid as

$$\begin{array}{l} CH_2 - CH.COOH \\ \quad\vert\qquad\vert \\ \quad\vert\quad C(CH_3)_2 \\ \quad\vert\qquad\vert \\ CH_2 - C(CH_3)(COOH) \end{array}$$

which is in accordance with Bredt's formula for camphor, which is $C_8H_{14}\begin{cases} CH_2 \\ \vert \\ CO \end{cases}$ when the complex C_8H_{14} is identical with that of camphoric acid.

Fenchyl Alcohol, $C_{10}H_{17}OH$.—This alcohol is isomeric with, and closely analogous to, borneol. It was originally prepared by Wallach by reducing the ketone fenchone, a natural constituent of several essential oils, by means of sodium. Later (*Annalen*, 1895, p. 324) he obtained it in fairly large quantities as a by-product in the preparation of fenchone-carboxylic acid, by passing a current of CO_2 through an ethereal solution of fenchone in the presence of sodium. Fenchyl alcohol, when quite pure, melts at 45° (not at 40°, as frequently stated). It boils at about 200°, and has a specific

gravity of ·933 at 50°. It is known in both optically active varieties, that prepared from dextro-fenchone being laevo-rotary, whilst laevo-fenchone yields dextro-fenchyl alcohol. The specific rotation is ± 10·6°. Inactive fenchyl alcohol melts at 35°, and results from mixing the two isomers. Dehydrating agents, such as potassium bisulphate, abstract water, with the formation of the terpene, fenchene. A liquid chloride is obtained by the action of phosphorus pentachloride, which boils at 85°, under a pressure of 16 mm., and has a specific gravity ·983.

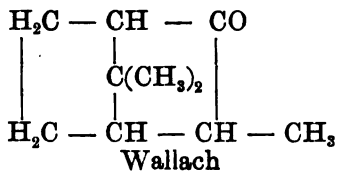
Schimmel & Co. have prepared an isomer of fenchyl alcohol, which they termed isofenchyl alcohol, by treating fenchene with sulphuric and acetic acids, and hydrolysing the resulting ester.

Isofenchyl alcohol melts at 62°, and boils at 98° at 13 mm. Its specific gravity at 15° is 0·9613, and its refractive index 1·48005 at 15°. Its optical rotation $[a]^{d}$ is − 25·73°.

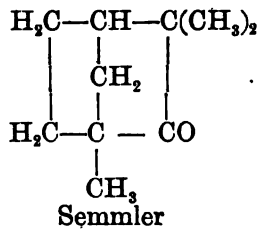
Fenchone, $C_{10}H_{16}O$.—This ketone occurs as dextro-fenchone in oil of fennel, and as laevo-fenchone in oil of thuja. It can be extracted in a pure state from either of these oils by treating the fraction boiling at 190° to 195° with nitric acid, and steam distilling the product. When purified, it forms an oil of camphoraceous odour, boiling at 193°, of specific gravity ·946 at 19°, and solidifying at low temperatures, after which it melts at + 5° to + 6°. Its optical rotation is ± 72° and refractive index 1·4631 at 20°. It can also be prepared by oxidising fenchyl alcohol, the optical activity being opposite in sign to that of the alcohol from which it is produced. The inactive form results from mixing equal quantities of the optically active varieties. On reduction, as above stated, it yields fenchyl-alcohol, $C_{10}H_{17}OH$. It forms an oxime, $C_{10}H_{16}NOH$, melting, when quickly heated, at 161°. Numerous other derivatives are known, which are

in many cases quite analogous to the corresponding camphor compounds.

The constitution of fenchone (and correspondingly of fenchyl alcohol) is still a matter of uncertainty. Up till quite recently Wallach's formula has been accepted as correct, but Semmler has thrown considerable doubt upon it. The suggested formulæ are as follows :—



Wallach



Semmler

Thujyl Alcohol, $C_{10}H_{17}OH$.—This body does not, apparently, occur in nature. It results from the reduction of its ketone, thujone, by means of sodium. It is identical with the body originally described by Semmler under the name tanacetyl alcohol. When pure it is a liquid boiling at 92° under a pressure of 13 mm., of specific gravity ·927. Its refractive index is 1·4635 at 20°. It yields a chloride, thujyl chloride $C_{10}H_{17}Cl$, by the action of phosphorus pentachloride, which on treatment with aniline yields up HCl, with the formation of the terpene thujene.

There are two, if not three, physically isomeric thujyl alcohols, which are identical in chemical structure. These correspond to the isomeric thujones described below.

Thujone, $C_{10}H_{16}O$.—This ketone, isomeric with those above described, is found in the oils of thuja, tansy, wormwood and sage. It is identical with the bodies formerly described under the names tanacetone and salvone. It is best prepared in a state of purity from oil of wormwood. According to Semmler, 200 c.c. of the oil, 200 c.c. of a saturated solution of sodium bisulphite, 75 c.c. of water, and 300 c.c. of alcohol

are well shaken at intervals during a fortnight. The crystals formed, consisting of the compound of thujone with the sodium bisulphite, are separated, washed with alcohol-ether and pressed. On treatment with caustic soda solution, the thujone, amounting to over 40 per cent. of the oil used, separates, and can be distilled with steam.

The hitherto unanswered question whether the chemically identical thujones isolated from various essential oils are also physically identical, or whether they are physically isomeric, has now been decided by Wallach in the last-named sense. He has succeeded in establishing the presence of two and possibly of three thujones, although with regard to the third the more probable view is, that it represents a mixture of the other two. His examination has moreover proved that thuja oil contains essentially *a*-thujone, and oil of tansy essentially *β*-thujone. Wormwood oil is very rich in *β*-thujone, but also contains some of the *a*-compound. Oils of artemisia and sage contain mixtures of *a*- and *β*- thujones. The formation of the semicarbazones and their fractional crystallisation from methyl alcohol afford means for the separation and identification of the isomers.

a-thujone is laevo-rotatory, and yields two semicarbazones, one dextro-rotatory, melting at 186° to 188°, and one, also dextro-rotatory, of the indistinct melting point 110°. Pure *a*-thujone has the following properties: boiling point, 200° to 201°; specific gravity, 0·912; $n_{d_{22^\circ}}$ 1·4503; $[a]_d$ −10·23°. *a*-thujone is partially converted into *β*-thujone when heated with alcoholic potash solution, formic acid, or alcoholic sulphuric acid. The last-named then effects a further conversion into isothujone (*q.v.*).

β-thujone is dextro-rotatory, but is not the optical antipode of *a*-thujone. The semicarbazone exists in a labile dextro-rotatory form of the melting point 174° to 176°, which readily passes over into the second form, melting at 170° to

172°. When mixtures of the semicarbazones of β-thujone or of α-thujone, or of both, are present, they give rise to complications which become even more pronounced owing to the fact that mixed crystals of uniform appearance are formed which can only be split up by very frequent recrystallisation. The ketone liberated from the semicarbazone by means of phthalic anhydride has the specific rotatory power [α] + 76·16°. Its oxime melts at 54° to 55°, and is dextro-rotatory. β-thujone can also be converted into the isomeric α-thujone by boiling with alcoholic potash.

The various compounds of this ketone are closely analogous to those of the isomers already described.

Thujone is easily converted into the isomeric ketones, isothujone and carvotanacetone. The former results by heating thujone with 40 per cent. sulphuric acid, whilst the latter is formed by heating thujone in a closed tube to 280°. The more interesting of these isomers is isothujone, for on reduction with sodium and alcohol, an alcohol $C_{10}H_{19}OH$ results, which is isomeric with menthol, and which is sufficiently similar to this body in its properties to be termed thujamenthol. Thujamenthol on oxidation yields the ketone thujamenthone, which is isomeric with ordinary menthone. Carvotanacetone yields corresponding compounds carvomenthol and carvomenthone. The physical properties of the isomers, thujone, isothujone and carvotanacetone are given by Wallach as follows:—

	Boiling Point.	*Specific Gravity.*	*Refractive Index.*
Thujone . .	200°-201°	·912	1·4503
Isothujone .	231°-232°	·9285	1·48217
Carvotanacetone	228°	·9378	1·48350

Tiemann gives the boiling point of thujone (tanacetone) as 203° and of carvotanacetone as 230°.

Terpineol, $C_{10}H_{17}OH$.—The substance usually known in commerce under this name, which now plays an important part in the preparation of artificial perfumes, has long been

a puzzle to chemists. Wallach prepared it by acting on terpin hydrate with dilute phosphoric acid. He stated that it was a monatomic alcohol, boiling at 215° to 218°, and described it as a liquid. Bouchardat and Tardy prepared it by the action of very dilute sulphuric acid on terpin hydrate, and found that it solidified on cooling and then melted at 30° to 32°, easily remaining in a state of superfusion. A closer examination by Wallach and Baeyer showed that the true melting point is 35°. A study of the two bodies, the "liquid" and the "solid" terpineol, and of their oxidation products, has revealed that there are at least twelve definite isomeric terpineols, capable of being synthesised. The liquid terpineol of commerce consists of a mixture of two of these, those melting at 35° and at 32° to 33°, with either some trace of impurity, or else a third isomeric liquid form. The terpineols possess an odour recalling hyacinths, hawthorn and lilac, and are largely used for the preparation of these perfumes. They are optically inactive, but Semmler has recently prepared optically active terpineols, by replacing the chlorine in the two limonene monohydrochlorides by the hydroxyl group. The resulting terpineol is optically active in the same direction as the limonene from which it is produced. Baeyer has, in addition, synthesised an *isomeric* terpineol, melting at 69° to 70°.

Terpineol melting at 32° to 33°, designated by Wallach β-terpineol, has a specific gravity at 15° = 0·923. It boils at 90° at 10 mm. pressure and 210° at 752 mm., and has a refractive index 1·4747 at 20°. Its phenylurethane melts at 85°. Its nitrosochloride melts at 102° to 103°.

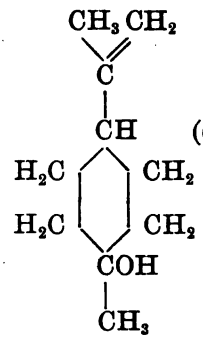
Terpineol melting at 35° to 36° has a specific gravity 0·939 at 15°. It boils at 98° at 10 mm., and at 219° at 752 mm. Its refractive index is 1·48132. Its phenylurethane melts at 112° to 113°.

Terpineol melting at 69° to 70° was prepared by Baeyer

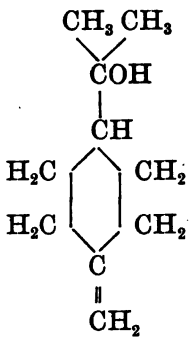
by reducing tribromoterpane with zinc and acetic acid. This results in an acetate of the alcohol, which yields the terpineol on hydrolysis. This melts at 69° to 70° and boils at 110° to 120° at 17 mm.

The relation between these three isomers is probably as follows:—

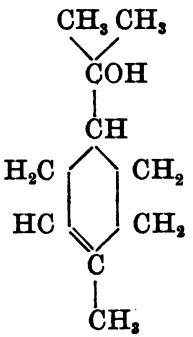
MELTING-POINT 32°-33°.



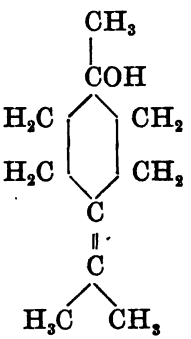
(or)



MELTING-POINT 35°-36°.



MELTING-POINT 69°-70°.



In addition to the artificially prepared, optically active terpineols (*e.g.*, by treating French turpentine with alcoholic sulphuric acid, etc.), such active terpineols are found in a few essential oils. Ceylon cardamom oil contains dextro-terpineol, $[a]_d = +83°$; oil of lovage also contains dextro-terpineol.

Terpineol occurs in the free state in the oil of *Erigeron canadense*, and as the acetate in cajuput and cardamom oils.

Pulegol, $C_{10}H_{17}OH$, is the alcohol corresponding to the ketone, pulegone, from which it can be obtained by reduction with sodium. It is a viscous liquid, having the odour of terpineol, boiling at 215°, of specific gravity ·912, but has not been obtained free from menthol, so that its properties are rather uncertain. Isopulegol, however, can be obtained by treating citronellal with acetic anhydride, when isopulegyl acetate results. The free alcohol, which corresponds to isopulegone, has a specific gravity 0·9154 at 17° and refractive index 1·4729. It is optically active, – 2·65°, and boils at 91° at 13 mm. pressure. The ketones themselves are, however, of chief interest.

Pulegone, $C_{10}H_{16}O$, occurs in the oils of *Mentha pulegium* and *Hedeoma pulegoides*. It is a liquid ketone, combining with sodium bisulphite to form a crystalline compound, which, when decomposed, yields the ketone in a pure state. It then boils at 221°, and has a specific gravity ·936, refractive index 1·4702 and optical rotation + 23°. It yields numerous characteristic derivatives, of which the oxime $C_{10}H_{16}NOH$ melts at 118°, and the semi-carbazone at 172°. When hydrolysed by means of formic acid pulegone yields acetone and methyl-cyclohexenone $C_7H_{12}O$. When this body is again condensed with acetone, it yields a body isomeric with, and very similar to, natural pulegone. This body may be termed pseudo-pulegone. A second isomer, isopulegone, was obtained by Tiemann and Schmidt, by oxidising isopulegol, a body which they obtained in the form of its acetate by heating citronellal (*q.v.*) with acetic anhydride. This isopulegone is probably a mixture of two stereoisomers which have not been separated. Isopulegone boils at 85°, under a pressure of 13 mm., has a specific gravity 0·921 at 18°, refractive index 1·4690 and optical rotation + 10° 15′. The pulegone and the isopulegone series of compounds are very similar in their physical and chemical properties, but they differ sharply in

the fact that natural pulegol and pulegone yield some menthol when reduced with sodium, whilst isopulegol and isopulegone resist the action of the metal. The properties of the isomers are compared in the following table:—

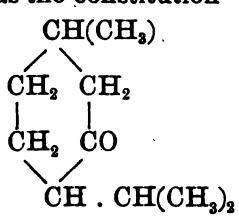
	Boiling Point.	*Specific Gravity.*	*Rotation.*	*Refractive Index.*
Pulegol . .	108° at 15 mm. 215° at 760 mm.	·912 at 20°	—	—
Isopulegol . .	91° at 12 mm.	·916 at 18°	− 2·7°	1·4729
Pulegone . .	99° at 12 mm. 221° at 760 mm.	·936	+ 22·9°	1·4702
Isopulegone .	85° to 90° at 13 mm.	·921 at 18°	+ 10·25°	1·4690
Pseudo-pulegone	94° at 14 mm. 215° at 760 mm.	·918 at 20°	dextro	1·4673

Sabinol, $C_{10}H_{15}O$.—Schimmel & Co. have shown that the principal constituent of savin oil is an alcohol of the formula $C_{10}H_{15}O_4$, which they have termed sabinol. It is a colourless oil, with an odour somewhat resembling thujone. Its specific gravity is 0·9432 at 20°, refractive index 1·4880, and boiling point 208° to 209°. It is probably a secondary alcohol, which is reduced to thujyl alcohol by treatment with sodium and amyl alcohol.

Menthol, $C_{10}H_{19}OH$.—This important compound is a crystalline alcohol, which occurs to a very large extent in oil of peppermint, from which it may be separated by freezing. It can also be prepared experimentally, from its ketone, menthone, and, with other bodies, from pulegone, by reduction. Menthol forms fine white crystals, melting at 43°, boiling at 212°, and having a specific gravity ·890 at 15°. When obtained from oil of peppermint it is laevo-rotary, about − 59°. Careful oxidation converts it into menthone, the corresponding ketone. Menthol has all the ordinary properties of an alcohol, and forms well-defined esters with the organic acids. Of these menthyl acetate, $C_{10}H_{19}O \cdot CO \cdot CH_3$, is of the most frequent occurrence in nature. It is a liquid of penetrating odour, boiling at 224°. The relations of menthol to menthone are the same as those of borneol to camphor, and there is a close similarity between many of their derivatives.

When menthone is reduced a mixture of dextro- and laevo-rotary menthols results, as well as an isomenthol, melting at 78° to 81° and of optical rotation + 2°. Numerous other isomers have been prepared by the reduction of ketones, etc., to which the names pulegonementhol, thymomenthol, etc., have been ascribed. These, however, rarely, if ever, occur in essential oils.

Menthone, $C_{10}H_{18}O$, occurs with menthol in oil of peppermint. According to the early work of Moriya, this body was described as optically inactive, but this has been shown to be incorrect. Atkinson describes it as an oily liquid, boiling at 206°, with a rotary power of + 21°. Beckman gives 208° as its boiling point, and 26° to 28° as its optical activity. Its specific gravity is ·894. Oxidation of natural menthol produces laevo-menthone, but this is easily converted into dextro-menthone by the action of acids. This, on reduction, yields dextro-menthol. The various derivatives of the optically active isomers correspond closely, but complicated stereochemical relationships exist, which render the chemistry of their derivatives a very difficult question. The oximes of the two isomers do not correspond in their properties, that of dextro-menthone being a laevo-rotary oil, whilst that of laevo-menthone is a solid, melting at 59°. The semicarbazone melts at 184° in both cases. There are numerous bodies isomeric with, and closely similar to, those of the menthone series. Those of the thujamenthol and carvomenthol series have already been mentioned. Menthone, in all probability, has the constitution—



menthol being, of course, the corresponding alcohol.

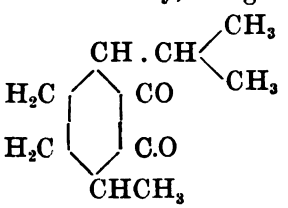
Four isomeric menthones may exist, with eight corresponding isomeric menthols (*vide supra*). But whichever menthone is converted into menthol, natural laevo-menthol is the predominating resulting compound. Menthone has been synthesised by Kötz and Hesse from methyl-hexanone and ethyl oxalate.

Cineol, $C_{10}H_{18}O$.—This body, which is somewhat isolated in its chemical relationships, may well be discussed here. It has been described under several names, the best known being that now usually adopted, *viz.*, cineol; also cajuputol (from its occurrence in oil of cajuput) and eucalyptol (from its occurrence in oil of eucalyptus). It is found in nature in very large quantities in the above-mentioned oils, as well as in many others, notably wormseed, lavender (English) and spike-lavender oils. It results also by the treatment of terpin hydrate with acids. Wallach and Brass, who first characterised it as a definite compound, gave the following method for its preparation. A current of dry hydrochloric acid gas is passed into rectified wormseed oil. The resulting crystalline magma of cineol hydrochloride is pressed at low temperature to remove as much as possible of adhering liquid, and the crystals are treated with water and steam distilled. The crude cineol is again subjected to this treatment when the pure body is obtained. When pure, cineol is an optically inactive liquid, solidifying at low temperatures and melting at - 1°, with a characteristic camphoraceous odour. It boils at 176°, and has a specific gravity ·930. Its refractive index is 1·4596. Scammell proposed its separation by means of a definite crystalline compound with phosphoric acid. This body has the composition $C_{10}H_{18}O \cdot H_3PO_4$. The use of phosphoric acid is the basis of the 1898 British Pharmacopœial test for cineol in essential oils.

Cineol forms a number of crystalline derivatives, amongst which may be mentioned the hydrobromide, $C_{10}H_{18}O$. HBr.,

melting at 56°, and the compound with iodol, $C_{10}H_{18}O \cdot C_4I_4NH$, which forms yellowish-green crystals, melting at 112°. It also forms a crystalline compound with resorcinol, which will be referred to under Eucalyptus oil. These are both useful for identifying cineol. According to all reliable observations, the oxygen atom in cineol does not possess alcoholic, ketonic, aldehydic or acid functions. Apparently it is quite indifferent, which accounts for the isolated nature, chemically speaking, of the compound. Its relationships are certainly chiefly with the terpenes. In commerce, this body finds considerable employment under its other name, eucalyptol.

Diosphenol.—This body is conveniently mentioned here, although it is a phenolic ketone of the formula $C_{10}H_{18}O_2$ or $C_{10}H_{16}O_2$. It is a constituent of certain Buchu leaf oils and is a crystalline compound melting at 82° and boiling at 232°. Its formula is extraordinary, being :—



It forms an oxime melting at 156° and a phenylhydrazone which can only be solidified at low temperatures. It has recently been synthesised by Semmler and Mackenzie (*Berichte*, 1906, 1158).

III. THE GERANIOL AND CITRONELLOL GROUP.

This group of bodies has attracted a great deal of attention from a number of well-known chemists during the past ten or twelve years, and although we now understand something of the chemical relationships of the various members of the group, much is still a matter of some uncertainty. The more important compounds in this category are of the same empirical composition as the members of the camphor group,

but are entirely different from them in their actual constitution. They belong, indeed, to the aliphatic or open chain series of compounds.

It will be convenient to study this group under the two headings—geraniol and citronellol, these being the most important of its members. From time to time, various observers have announced the discovery and separation of aromatic alcohols (*i.e.*, *sweet smelling*, not belonging to the *aromatic* series) in certain essential oils, notably those of rose, geranium, neroli, citronella, linaloe, bergamot, lavender, limes, basil, petit-grain, coriander, and cananga, of the formula $C_{10}H_{18}O$. In general the properties of these alcohols were very similar, although not, in many cases, identical. Nerol is a well-defined and recently discovered isomer. Exhaustive and very thorough investigations, chiefly by Tiemann and Semmler, have gone far to prove that they are in nearly every case more or less impure forms of two chemical individuals. These are geraniol and linalol which we shall discuss immediately.

A short summary of some of the other alcohols whose claims to chemical individuality are now practically abandoned will, however, be useful. Aurantiol was announced by Semmler and Tiemann to exist as an acetate in oil of petit-grain. Its specific gravity was given by them as ·869 at 20°; it combines with four atoms of bromine; is laevo-rotary; refractive index 1·4682. Later on the same chemists agreed that this body was slightly impure linalol.

Coriandrol, announced by Barbier, was found in oil of coriander. Its properties were given as follows: boiling point, 196° to 198°; specific gravity at 0°, ·882; refractive index, 1·4640; rotary power, + 15° 1′. Barbier considered that this was dextro-rotary licareol. The latter was found in the oil of *licari kanali*, and its properties were almost exactly identical with those of coriandrol, except that its

optical activity was of the opposite sign. By the action of acetic anhydride, an acetate is formed, which Barbier claimed yielded a fresh alcohol, licarhodol, on saponification. This, he urged, was a stable isomeride of licareol. Bertram, however, in 1894, stated that licarhodol was merely geraniol, but Stephan has recently (*Jour. prakt. Chem.*, 1898, p. 111) shown that it also contains active terpineol. Bourchardat also claimed that licareol was identical with linalol.

Nerolol, obtained from oil of neroli, was speedily recognised by Tiemann as identical with linalol, but nerol has been established as a definite compound (*q.v.*).

Rhodinol was announced by Eckart to be an essential ingredient of Turkish and German rose oils. He regarded it as an unsaturated open chain alcohol. Markovnikoff thereupon urged that roseol, $C_{10}H_{20}O$, was the chief ingredient of rose oil, and much controversy has gone on between a number of continental chemists, as to the real identity of the body. Bertram, in 1894, claimed that it was in reality merely geraniol, but in 1896 Tiemann and Schmidt showed that the alcohols of rose oil consisted of a mixture of geraniol and citronellol, $C_{10}H_{20}O$, which latter body had evidently been mistaken for the so-called "rhodinol" and "roseol".

The names geraniol and citronellol therefore appear to be those most entitled to remain in chemical literature. Poleck, however, complains that the name geraniol has been substituted for the earlier rhodinol, overlooking the fact that the old rhodinol is clearly a mixture. Erdmann further complicates this matter by insisting on treating geraniol of commerce as a more or less impure body of which the principal constituent, $C_{10}H_{17}OH$, is called rhodinol, claiming that geraniol (pure) and rhodinol are identical, and that the former should be expunged from chemical literature. But the mass of evidence is in favour of the retention of the

name geraniol, and it is to be hoped that the polemics now obtaining in regard to this question have now ceased.

The last of these doubtful bodies to be mentioned is reuniol, found in various geranium oils (Réunion, African and Spanish) by A. Hesse. This had previously been announced as a probable chemical individual by Barbier, but he stated that he had not obtained it pure. Erdmann and Huth claim that it is more or less pure rhodinol, that is, geraniol.

Geraniol, $C_{10}H_{18}O$, is thus the most important alcoholic constituent of this group of essential oils. It is a colourless oily liquid, of pleasant rose-geranium odour, but lacking the fine character of the oils in which it occurs. It possesses the following properties. It boils at 229° to 230° under ordinary pressure, and at 120° under a pressure of 16 mm. Its specific gravity is about ·881, and its refractive index about 1·4780. It is optically inactive. By means of its refractive index (Brühl's theory), and its ready combination with four atoms of bromine, it is shown to contain two ethylene unions, hence it cannot be a closed chain compound. By careful oxidation with chromic acid it yields its aldehyde, citral (*q.v.*), and by heating in an autoclave with water to 200° it is partly converted into its isomer, inactive linalol. It yields an acetate when acted upon by acetic anhydride, which also occurs in nature. This is a fragrant oil, of specific gravity ·9174, and refractive index 1·4628, boiling at 128° to 129° under a pressure of 16 mm. It occurs naturally in several essential oils.

To purify geraniol and separate it in a state of absolute purity, Tiemann and Kruger recommend dissolving sodium in the alcohol, treating the sodium alcoholate with ether and phthalic anhydride; the resulting geraniol sodium phthalate is hydrolysed by alcoholic potash, and the pure geraniol precipitated by the addition of water.

To detect geraniol in essential oils, Jacobsen recommends the following process, provided that the amount present exceeds 25 per cent. The dry oil is intimately mixed with an equal weight of dry powdered calcium chloride, and the mixture kept in a desiccator at – 4° for twelve to sixteen hours. The soft mass is rubbed up with dry benzene, ether, or petroleum ether, and the liquid portion removed by a suction filter. The calcium chloride compound of geraniol is then treated with water, and the oil separated, washed and distilled, when geraniol passes over at 228° to 230°. Another useful method for its identification, which was discovered by Erdmann, consists in heating the alcohol with diphenylcarbamine chloride and pyridine in a water bath. Unaltered products and diphenylamine are removed by steam distillation, and the residue crystallised from alcohol. The pure geraniol diphenylurethane resulting, crystallises in colourless needles, melting at 83°. An ethereal pseudo-salt, which forms crystals melting at 49°, has recently been described by Erdmann. It is obtained by heating the alcohol with opianic acid, when the two bodies combine to form the crystalline compound. According to Tiemann and Semmler, who have worked for many years on geraniol, its constitution is—

$$(CH_3)_2C : CH . CH_2 . CH_2 . C(CH_3) : CH . CH_2OH.$$

Linalol, $C_{10}H_{18}O$, is isomeric with geraniol, but, as it is known in both the optically active forms, as well as in the inactive, it is certainly not a stereoisomer of this body. It was first discovered in oil of linaloe, of which oil it is the most important constituent. It is a pleasant-smelling liquid, and occurs both free and combined as the acetate, in various oils, notably those of linaloe, lavender and bergamot. It is an oily liquid, boiling at normal pressure at about 198°, and at 86° to 87° at 14 mm. Its specific gravity is ·872 at 15·5°, and refractive index 1·4630. These figures are from a specimen obtained from licari oil. A sample from linaloe

oil gave a higher specific gravity, *viz.*, ·8765 at 17·5°. The optical activity is not known with certainty. Probably it is about ± 20°. On oxidation it yields, amongst other products, geranaldehyde. Bouchardat states that if linalol is treated with acetic anhydride at low temperatures, an acetate is formed, which regenerates linalol on hydrolysis, but that at elevated temperatures a new alcohol is formed. This, however, has since been shown to be a mixture of geraniol and terpineol. Linalyl acetate, $C_{10}H_{17}O \cdot COCH_3$, is the important constituent of bergamot oil, and occurs in many other oils also. It is an odoriferous liquid of specific gravity ·912, boiling at 105° to 108° at 11 mm. It can be prepared by the action of acetate anhydride on linalol. Its close connection with geraniol, together with a study of its derivatives, cause Tiemann and Semmler to assign to linalol the formula :—

$$CH_3 \cdot C(CH_3) : CH \cdot CH_2 \cdot CH_2 \cdot C(CH_3)(OH) \cdot CH : CH_2.$$

Nerol, $C_{10}H_{17}OH$.—This alcohol was discovered by Hesse and Zeitschel in neroli and petit-grain oils by freeing the oil as far as possible from geraniol and then preparing diphenylurethanes of the residuary mixed alcohols. By fractional crystallisation the nerol compound can be obtained in a state of purity, and the alcohol is obtained by saponification in the usual manner. Nerol has a specific gravity 0·8813, is optically inactive, and boils at 224° to 225° at 755 mm. and at 125° at 25 mm. The diphenylurethane melts at 52° to 53° (that of geraniol melts at 81°) and the tetrabromide at 118° to 119°. Nerol is almost certainly a stereoisomer of geraniol, related to it as shown by the appended formulæ, and their corresponding aldehydes are probably the *α*-citral (= geranial) and *β*-citral (= neral) :—

geraniol.

$$CH_3 . C . CH_2 . CH_2 . CH : C(CH_3)_2$$
$$\|$$
$$CH_2(OH)C . H$$

a-citral

$$CH_3 . C . CH_2 . CH_2 . CH : C(CH_3)_2$$
$$\|$$
$$CHO . C . H$$

nerol

$$CH_3 . C . CH_2 . CH_2 . CH : C(CH_3)_2$$
$$\|$$
$$HC : CH_2OH$$

β-citral

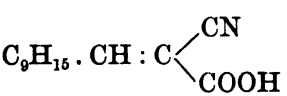
$$CH_3 . C . CH_2 . CH_2 . CH : C(CH_3)_2$$
$$\|$$
$$HC . CHO$$

Geranaldehyde, $C_{10}H_{16}O$. — This body, which has been long known as the aldehyde of geraniol, and is known generally by the name citral, occurs to a considerable extent in many oils of the *Citrus* family. It is highly odoriferous, and is, to a great extent, responsible for the perfume of several oils. Lemon oil, the oil of *Backhousia citriodora* and lemon-grass oil all contain citral, the two last named in considerable proportion. It can also be obtained by the oxidation of the alcohols geraniol, and nerol or linalol, by means of chromic acid. To prepare it from this source, 10 grammes of potassium bichromate are dissolved in a mixture of 12·5 grammes of sulphuric acid and 100 grammes of water; 15 grammes of geraniol are then added. The mixture should be kept well cooled at first, and allowed to become warm afterwards, and well shaken for half an hour. It is then rendered slightly alkaline, and distilled in a current of steam. To separate the aldehyde from other products, the distillate is mixed with a saturated solution of sodium bisulphite, and allowed to stand for twenty-four hours, with occasional shaking. It forms a crystalline compound with the bisulphite, which is separated, pressed between blotting paper, washed

with ether, and mixed with sodium carbonate, and steam distilled. Citral can also be obtained from essential oils, such as lemon-grass oil, by means of the bisulphite process, but care should be taken that the temperature be kept low, as otherwise a considerable loss occurs, due to the conversion of part of the citral into sulphonic acid compounds. Pure citral boils at about 228° to 230° under ordinary pressure, and at 110° under a pressure of 12 mm. It is an oily liquid of specific gravity ·8972, and refractive index 1·4931, but optically inactive. It combines with 4 atoms of bromine, and, under the influence of dehydrating agents, such as potassium hydrogen sulphate, yields cymene, $C_{10}H_{14}$. Under the influence of alkalies, citral condenses with acetone, with the splitting off of water to form pseudo-ionone, $C_{13}H_{20}O$, which is converted into isomeric ionones by means of acids. These bodies are the characteristic artificial violet perfume, which will be mentioned later. Reduction with sodium and alcohol produces the alcohol, geraniol. Various derivatives of citral have been prepared, such as the oxime, anilide and phenylhydrazone, which are oily liquids, and the semicarbazone, which appears to exist in several isomeric forms of different melting points. Most characteristic, however, is the citryl-β-naphtocinchonic acid, discovered by Doebner. This can be prepared by warming together in alcoholic solution 20 parts of citral, 20 parts of β-naphthylamine and 12 parts of pyruvic acid. This acid, $C_{23}H_{23}NO_2$, melts sharply at 197°, and is the most useful compound for characterising citral. Indeed, Doebner has applied its preparation to the quantitative estimation of citral in oils containing it. The determination of this body in essential oils is by no means an easy matter, and will be mentioned later. A study of citral and its derivatives has caused the most recent investigators to assign the formulæ given on page 55 to the stereoisomeric varieties of citral.

Several years ago Tiemann carried out a great deal of work on the chemistry of citral (*Berichte*, xxxi., pp. 3278, 3324; xxxii., p. 107), in connection with which the following points are especially noteworthy. He has shown that in addition to the normal bisulphite of sodium compound of citral, three hydrosulphonic acid derivatives are formed, according to the conditions under which the experiment is performed (acidity, alkalinity, temperature, etc.). He attempted to explain the existence of two well-defined isomeric semicarbazones (melting at 164° and 171°) by suggesting that two stereoisomeric forms of citral are present in lemon-grass oil. To support this, he mixes the normal bisulphite compound with water and adds sodium carbonate. The liquid is then shaken with ether, and about half the citral is set free and dissolves in the ether (fraction *a*); the remainder is set free by the addition of caustic alkali and extracted with ether (fraction *b*). Whilst both fractions have exactly the same physical properties, it is found that fraction *a* gives only one semicarbazone, melting at 164°, whilst fraction *b* gives both, melting at 164° and 171° respectively. The same was found to be the case with the cyanacetic compound, fraction *a* yielding only one citralidene cyanacetic acid melting at 122°, whilst fraction *b* gave this, and also one melting at 80°. This view has been confirmed by the discovery of the alcohol nerol, as mentioned above (see also under ionone).

Professor Tiemann has also shown that by condensation of citral with cyanacetic acid, a citralidene cyanacetic acid



is formed which crystallises in fine needles, and melts at 122°. This compound is very well adapted for the detection of citral in essential oils. The behaviour of citral towards semicarbazide has also been used for the detection of the

aldehyde, without, however, giving a satisfactory result, because mixtures of semicarbazones with different melting points (130° to 170°) are formed.

The stereoisomeric form of citral as prepared by Tiemann had the following characters:—

	Citral a.	*Citral b.*
Specific gravity . .	0·8898	0·888
Boiling point (20 mm.)	118°-119°	118°
Refractive index at 20°	1·4891	1·49001

For the quantitative determination of citral in lemon-grass oil the use of indirect methods is preferable. The aldehyde is converted into the normal, slightly soluble sodium bisulphite compound, by agitating the oil with sodium bisulphite solution or by the action of sodium sulphite and sodium bicarbonate, into sodium citraldihydro-disulphonate. The non-aldehydic compounds are separated from the citral-derivatives formed by agitation with ether, and are measured in a suitable tube or are weighed after the evaporation of the solvent. The difference between the oil used for the determination and the non-aldehydes represents approximately the amount of citral.

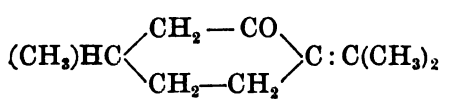
In practice concordant results are obtained in the case of oils with high citral values, by agitating the oil repeatedly with a 30 per cent. hot solution of sodium bisulphite in a water bath for an hour and allowing to stand in suitable flasks with graduated necks, when the non-aldehydes can be read off. Other processes will be referred to later.

Citronellol, $C_{10}H_{20}O$, is an alcohol closely related to geraniol. It was first obtained by Dodge, by reducing the aldehyde citronellal, $C_{10}H_{18}O$, by means of sodium amalgam and acetic acid. Later Tiemann and Schmidt showed that the alcoholic constituents of oil of roses consisted of geraniol and citronellol. Spanish geranium oil also contains citronellol, in both the *dextro-* and the *laevo*-rotary

forms. It is an odoriferous oil, boiling at 117° to 118° under a pressure of 17 mm., has a specific gravity ·8565 at 17·5°, and a refractive index 1·4566; its specific rotary power is about 4°. Citronellol, obtained by reducing the aldehyde, is dextro-rotary; that from oil of roses is laevo-rotary, whilst in most geranium oils both varieties exist. It forms an acetate, an oily liquid of characteristic odour, of specific gravity ·8928 at 17·5°, boiling at 120°, under a pressure of 15 mm., and with an optical activity $[\alpha]_d = 2·4°$ and refractive index 1·4456.

A number of characteristic derivatives have been prepared and described by Semmler. The oxime, $C_{10}H_{18}NOH$, boils at 135° to 136° under a pressure of 14 mm., and has a specific gravity ·9055 at 20°. Citronellic acid, $C_{10}H_{18}O_2$, obtained by the action of silver oxide and ammonia on the aldehyde, boils at 143° under a pressure of 10 mm., and at 257° at 760 mm. Its specific gravity is ·9308 at 20°. The stereoisomeric relationships of the two forms of critonellol are demonstrated by the fact that they both yield β-methyl-adipic acid when oxidised; this, however, is *dextro-* or *laevo*-rotary, according to the activity of the citronellol from which it is produced.

Although belonging to the closed-chain series of compounds, several members of the menthone group are very closely related to the bodies just described. Tiemann obtained a closed-chain alcohol, isopulegol, $C_{10}H_{18}O$, by heating citronellal with acetic anhydride in an autoclave. This, on oxidation with chromic acid, yields isopulegone, $C_{10}H_{16}O$, the corresponding closed-chain ketone, isomeric with natural pulegone (the characteristic constituent of oil of pennyroyal), which is probably of the constitution—



By acting on isopulegone with barium hydroxide, it is completely converted into ordinary pulegone.

Wallach has succeeded in reversing the change, and has prepared from menthone (the ketone corresponding to menthol, and a body closely allied with pulegone) an open-chain compound which he calls mentho-citronellol. Menthone, $C_{10}H_{18}O$, is converted into its oxime, $C_{10}H_{18}.N.OH$, which when heated with phosphoric anhydride yields the corresponding nitrile $C_9H_{17}.CN$. On reduction this gives menthonylamine $C_9H_{17}.CH_2.NH_2$, and this, by the action of nitrous acid, gives mentho-citronellol, according to the equation—

$$C_9H_{17}.CH_2.NH_2 + NO.OH = C_9H_{17}.CH_2OH + N_2 + H_2O.$$

Menthonylamine. *Mentho-citronellol.*

Wallach assigns to this body the same constitution as that attributed to citronellol by Tiemann and Schmidt, *viz.*, $C(CH_3)_2 : CH . CH_2 . CH_2 . CH(CH_3) . CH_2 . CH_2 . OH$. On oxidation this body yields mentho-citronellal $C_9H_{17}.COH$, but this is not identical with ordinary citronellal. The relations between the ordinary citronellol series and these new bodies require further explanation.

The frequent occurrence of citronellal and citral, and of citronellol and geraniol, together in essential oils makes it a matter of some importance to be able to effect a separation of the bodies. For the former case Doebner gives the following method. The oil is digested with pyruvic acid and β-naphthylamine, when condensation products of the aldehydes with β-naphtho-cinchoninic acid are formed. The citral compound is less soluble than the other and therefore crystallises out. The citronellal compound melts at 215° (whilst that of mentho-citronellal melts at 214°, which proves that they are not identical).

Flatau and Labbé have published a method for the separation of citral from citronellal which depends upon the fact that the aqueous solution of the sodium bisulphite

compound of citral gives no precipitate with barium salts, while the insoluble barium compound of citronellal is quantitatively precipitated. The separation of a mixture of both aldehydes is effected in the following way. Firstly, the normal sodium bisulphite compound of the aldehydes is prepared and dissolved in water; this is precipitated by barium chloride and the precipitate of the citronellal compound is collected upon a filter. From the filtrate, the citral is isolated by the addition of alkali, and by shaking the fluid with ether. The barium sulphite compound of citronellal is agitated with alcoholic potash, avoiding heating, and is separated by filtration from the barium and potassium sulphites formed. In order to remove the excess of alkali, the filtrate is saturated with carbonic acid gas, once more filtered, and the citronellal, separated from the solution by the addition of water and taken up by ether. By means of this method, Labbé claims to have obtained besides 70 per cent. of citral, 6 per cent. of citronellal from oil of lemon-grass. In the same way citronella oil was found to contain 25 to 30 per cent. of citronellal, and 2 to 5 per cent. of citral. These results are, however, of doubtful value as this method is not very reliable.

To separate citronellol and geraniol Tiemann and Schmidt heat the liquid with an equal weight of phthalic anhydride to 200° for about two hours. Geraniol is thus converted into a hydrocarbon, while citronellol is converted into a phthalic acid compound, which is shaken out with dilute potash and washed free from hydrocarbons with ether, and hydrolysed. The citronellol is thus set free. The same chemists have succeeded in separating citronellol when occurring in very small proportion in geraniol, by a method depending on the conversion of the citronellol into its phosphate and then separating this. Briefly, the method consists in acting on the mixture of geraniol and citronellol with phosphorus trichloride, using ether as the solvent. 100 parts of the

alcohols in 100 parts of absolute ether are cooled to − 10° and gradually added to 60 parts of phosphorus trichloride in 100 parts of ether, also cooled to − 10°. The temperature must not rise above 0° till the mixture is complete. It is then allowed to stand for four to five days at the ordinary temperature. The ethereal solution is then mixed with powdered ice and washed with ice water. After a second washing with ice water, it is washed with solution of soda which extracts a citronellyl-phosphoric acid, leaving geranyl chloride in the ether. The aqueous solution of the sodium salt of the citronellyl-phosphoric acid is washed with ether, and then saponified with strong alkali, and the citronellol distilled over with steam.

The probable constitution of citronellol is :—

$C(CH_3)_2 : CH . CH_2 . CH_2 . CH(CH_3) . CH_2 . CH_2 OH.$

Citronellal, $C_{10}H_{18}O$, is the aldehyde of citronellol, and occurs in several essential oils, notably in citronella oil, in which it was first discovered by Dodge, who separated it by means of its bisulphite compound. It is an oily liquid of characteristic odour, of specific gravity ·8768 at 17·5°, and refractive index 1·4481. Natural citronellal is usually dextrorotary, from + 8° to + 12°. On reduction it yields the alcohol, citronellol, $C_{10}H_{20}O$. It boils at 205° to 208° under ordinary pressure. It forms numerous characteristic derivatives, of which the oxime $C_{10}H_{18} . NOH$ is an oil boiling at 135° at 14 mm., of specific gravity ·906. It also forms a compound with phosphoric acid, which combines with aniline, the resulting salt melting at 165°. It appears almost certain that citronellol and citronellal are dihydro-derivatives of geraniol and geranial (citral). Citronellal has in all probability the constitution—

$C(CH_3)_2 : CH . CH_2 . CH_2 . CH(CH_3)CH_2 . COH.$

Methyl-heptenone, $C_8H_{14}O$.—This body is an open-chain ketone of the constitution $CH_3.C(CH_3) : CH.CH_2.CH_2.CO.CH_3$,

according to Tiemann. It occurs naturally in oil of lemon-grass and other oils, and results from the oxidation of citral, or the distillation of cineolic anhydride. Many discordant statements have been made as to the identity or otherwise of this ketone when extracted from different oils, but Tiemann's recent work tends to prove that natural methyl-heptenone has the formula given it above and is identical with that obtained from cineolic anhydride. It is best identified by its semicarbazone melting at 136° to 138°. It has a specific gravity 0·853 at 20°, boils at 173° to 174°, and has a refractive index 1·4439 at 15°.

THE GERANIOL AND CITRONELLOL SERIES.

	Boiling Point.	Sp. Gravity.	Refractive Index.	Optical Activity.	B. P. of Acetate.	Sp. Gr. of Acetate.
Geraniol $C_{10}H_{17}OH$	229°-230°	·880-·883	1·4776	inactive	128°-129° at 16 mm.	·9174 at 15°
Nerol $C_{10}H_{17}OH$.	226°-227°	·881	1·4776	„	—	—
Linalol $C_{10}H_{17}OH$.	195°-198°	·872	1·4630 at 20°	about ± 20°	105°-106° at 11 mm.	·912 at 15°
Citronellol (dextro) $C_{10}H_{19}OH$ . .	117°-118° at 17 mm.	·856 at 17·5°	1·4566 at 20°	+ 4°	119°-121° at 15 mm.	·893 at 17·5°
Citronellol (laevo) $C_{10}H_{19}OH$ . .	113°-114° at 15 mm.	·861 at 20°	1·4579 at 20°	- 4·3°	—	—
Citral (geranaldehyde) $C_{10}H_{16}O$.	228°-229°	·897 at 15°	1·4931 at 15°	inactive	—	—
Citronellal (dextro) $C_{10}H_{18}O$ . .	205°-208°	·875 at 17·5°	1·4481 at 20°	+ 8·2°	—	—
Citronellal (laevo) $C_{10}H_{18}O$ . .	148°-144° at 14 mm.	—	1·4536 at 20°	- 6·25°	—	—

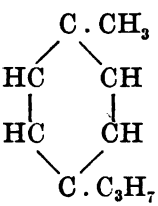
IV. BENZENE COMPOUNDS.

A large number of compounds, belonging to what is usually termed the *benzene series*, occur in essential oils. Comparatively few, however, are of common occurrence, and these are mainly either phenols or alcohols and their

immediate derivatives, aldehydes or acids. Of bodies outside these limits, the hydrocarbon cymene is probably that of most frequent occurrence. The following paragraphs deal briefly with the most important of these bodies:—

Cymene.

Cymene, $C_{10}H_{14}$.—There are a number of isomeric bodies of this formula, which are either propyl-methyl-, or isopropyl-methyl-benzene. That which is usually known as cymene, however, and which occurs, for example, in Roman caraway oil, is the *para*-methyl-isopropyl-benzene, that is, the isomer in which the methyl and the propyl groups are in the positions 1 and 4, acccording to the usually accepted notation for benzene derivatives. This body, then, has the constitution—



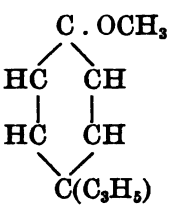
It is a pleasant-smelling liquid, boiling at 175° to 176°; of specific gravity ·8722 at 0°. It can be obtained by distilling camphor and phosphorus pentoxide, or by boiling cumic alcohol with zinc dust; or by heating *para*-bromtoluene with sodium and propyl iodide.

PHENOLS AND THEIR DERIVATIVES.

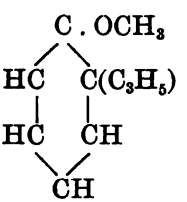
Phenols with Nine Carbon Atoms.

Chavicol, $C_9H_{10}O$, is the only nine-carbon phenol of note which is found naturally in the free state in essential oils. It is *para*-allyl phenol, of the constitution $C_6H_4(OH)(CH_2.CH:CH_2)$. It occurs in the oil of *Chavica Betle*, and is a colourless oil of strong odour, of specific gravity 1·035 at 20°, boiling at 237°. It yields no colouration with ferric

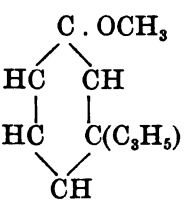
chloride. It yields a series of ethers, such as methyl- and ethyl-chavicol. The phenol *Anol* is very closely related to chavicol, being *para*-propenyl phenol, $C_6H_4(OH)(CH:CH.CH_3)$. It occurs naturally only in the form of ethers, the chief of these being *anethol*, $C_{10}H_{12}O$, which is its methyl ether, of the constitution $C_6H_4(O.CH_3)(C_3H_5)$. This body occurs in oil of aniseed, from which it can be separated in the form of white shining scales, melting at 21°, and boiling at 232°. It has been prepared synthetically from *p*-methoxyphenylcrotonic acid. It also results by means of a reaction common to this group of phenols. Methyl chavicol, above described, contains the allyl group, whilst anethol contains the propenyl group. It has been found that nearly all *allyl-benzene* derivatives are transformed into the isomeric *propenyl-benzene* derivatives, when heated with alcoholic potash. Methyl-chavicol in this way yields anethol. In this group of natural compounds the *propenyl* derivatives usually have higher specific gravities and boiling points than the corresponding *allyl* derivatives. Anethol is characterised by the formation of a brom-anethol dibromide, $C_6H_3Br.(OCH_3)(C_3H_5Br_2)$, melting at 107°. Compounds isomeric with anethol, in which the propenyl and the phenolic groups are in the *ortho*- and *meta*-positions, have been prepared by acting on the *ortho*- and *meta*-salicylic aldehydes with propionic anhydride and sodium propionate. The relations of these to natural anethol are shown in the following diagrammatic formulæ :—



Natural Anethol.



Ortho-Anethol.



Meta-Anethol.

Allyl-dioxybenzene, $C_9H_{10}O_2$, is capable of existing in six possible isomeric forms. Of these only one is of any importance, and that only in the form of its ethers. *Eugenol*, *chavibetol* and *safrol* are all derivatives of the phenol—

$$C_6H_3\begin{cases}C_3H_5 & (1)\\ OH & (3)\\ OH & (4)\end{cases}$$

when C_3H_5 is the allyl group, and the numbers refer to the position of the radicles in the benzene nucleus.

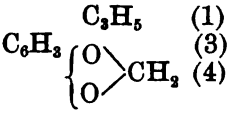
Estragol occurs in tarragon oil (estragon oil). It is isomeric with methyl chavicol and boils at 215°. It is converted into anethol by boiling with alcoholic potash.

Eugenol, $C_{10}H_{12}O_2$, is its methyl ether of the constitution $C_6H_3(C_3H_5)^1(OCH_3)^3(OH)^4$. It occurs in the oils of cloves, allspice, bay, and cinnamon leaves, and is a body of enormous commercial interest, on account of its use for the manufacture of vanillin (*q.v.*). It can be obtained in a state of comparative purity by shaking oil of cloves with alcoholic solution of potassium hydroxide. The whole solidifies to a crystalline mass. This is pressed, washed with alcohol and decomposed with an acid. The resulting oil, when washed to free it from traces of acid, can be purified by distillation. It is then a nearly colourless oil, of specific gravity 1·070, and refractive index 1·5400 and boiling at 247°. It is coloured blue by ferric chloride. By oxidation with potassium permanganate, it is converted into vanillin and allied bodies. Various ethers of eugenol also exist, methyl-eugenol, $C_6H_3(OCH_3)_2(C_3H_5)$, being a constituent of several essential oils. It can also be formed synthetically by the action of potash and methyl iodide on eugenol. Eugenol behaves in the manner above referred to when treated with hot alcoholic alkali, that is, it is converted into the corresponding propenyl compound, isoeugenol.

Chavibetol, $C_{10}H_{12}O_2$, is very closely related to eugenol, differing from it only in that the *hydroxy-* and the *methoxy-*

groups are in the reversed positions. It is a methyl ether of allyl-dioxy-benzene, of the formula $C_6H_3(C_3H_5)^1(OH)^3(OCH_3)^4$. It occurs with chavicol in oil of betel.

Safrol, $C_{10}H_{10}O_2$, is the methylene ether of allyl-dioxy-benzene, of the constitution—



It is found to a considerable extent in oils of sassafras, camphor, and *Ilicium religiosum*. When pure it is a white crystalline mass at low temperatures, melting at + 8°. At ordinary temperatures it forms a colourless oil of characteristic, pleasant odour, of specific gravity about 1·1, and boiling at 232°. It is optically inactive when pure. It is easily converted into isosafrol (containing the propenyl group) by the action of alcoholic potash. Safrol is used to an enormous extent for perfuming cheap soaps, and is also of great commercial value on account of the fact that on oxidation it yields heliotropin, an artificial perfume which is now largely employed (*q.v*).

Propenyl-dioxybenzene, $C_9H_{10}O_2$, is a phenol analogous in every respect to allyl-dioxybenzene. The difference between the two bodies is that the latter contains the allyl group . CH_2 . CH : CH_2, whilst the former contains the propenyl radicle . CH : CH . CH_3.

Isoeugenol, $C_{10}H_{12}O_2$, and *isosafrol*, $C_{10}H_{10}O_2$, are the two best known derivatives of this phenol. Isoeugenol results, according to the general rule of phenols containing the allyl group, when eugenol is boiled with alcoholic potash. It is also obtained by distilling homoferulic acid with lime. It is an oil boiling at 260°. Its constitution is identical with that of eugenol, $C_6H_3(C_3H_5)^1(OCH_3)^3(OH)_4$, except that C_3H_5 here represents the propenyl group. Isosafrol, $C_{10}H_{10}O_2$, is obtained in the same manner from safrol, *viz.*, by boiling

it with alcoholic potash. It is an oil, boiling at 248°, and solidifying at very low temperatures. Oxidation yields chiefly piperonal (artificial heliotropin).

Propenyl-trioxybenzene, $C_9H_{10}O_3$, is represented by its trimethyl ether, of the constitution $C_6H_2(C_3H_5)(OCH_3)_3$, asarone. This forms the solid constituent of the oil of *Asarum Europæum* and occurs in monoclinic prisms, melting at 61° and boiling at 295° to 296°. Its specific gravity at 18° is 1·165. This constitution has quite recently received definite confirmation by the synthesis of the body by Gattermann, who condensed oxyhydrokinone-trimethyl ether and hydrocyanic acid in benzene solution, by means of aluminum chloride, and treated the reaction product with water. Asaraldehyde resulted, of the formula $C_6H_2\begin{cases}(OCH_3)_3\\COH\end{cases}$, which was condensed with propionic anhydride and sodium propionate. Asarol, $C_6H_2\begin{cases}(OCH_3)_3\\CH:CH.CH_3\end{cases}$, identical with the natural body resulted (*Berichte*, 1899, p. 290).

Myristicene is butenyl-trioxybenzene-methyl methylene ether, $C_6H_2(C_4H_7)(CH_2O_2)(CH_3O)$. It occurs in the high boiling fractions of mace and nutmeg oil. It melts at 30°.

Allyl tetroxybenzene, $C_6H(C_3H_5)(OH)_4$, is represented by its dimethyl-methylene ether, *apiol*, $C_{12}H_{14}O_4$. Two isomers of this constitution, differing only in the relative positions of the substituent groups in the benzene nucleus, are well known, *viz.*, apiol from oil of parsley, and dill-apiol from some varieties of dill oil. The corresponding propenyl compounds, in which the allyl group is replaced by the propenyl radicle, are also known. Apiol from oil of parsley is a crystalline solid, volatile with steam, melting at 30° and boiling at 294°. It dissolves in strong sulphuric acid with a characteristic blood-red colour. By boiling it with alcoholic

potash the allyl group suffers rearrangement, and isoapiol, the isomeric methylene-dimethyl ether of propenyl-tetroxybenzene, results. This is also a crystalline solid, forming leaflets melting at 56° and boiling at 304°. In 1896 Ciamician and Silber announced the discovery of an isomeric apiol, which they separated from the high boiling fractions of oil of dill. It is an oily liquid, boiling at 285° with slight decomposition. When boiled with alcoholic potash it yields isoapiol, which differs from it in containing the propenyl instead of the allyl group. This body melts at 44° and boils at 296° with slight decomposition. A close study of these bodies has made it clear that the two isomeric apiols possess the formulæ—

$$C_6H\begin{cases}OCH_3\ (5)\\ O_2CH_2\ (4\text{ and }3)\\ OCH_3\ (2)\\ C_3H_5\ (1)\end{cases} \qquad C_6H\begin{cases}O_2CH_2\ (5\text{ and }4)\\ OCH_3\ (3)\\ OCH_3\ (2)\\ C_3H_5\ (1)\end{cases}$$

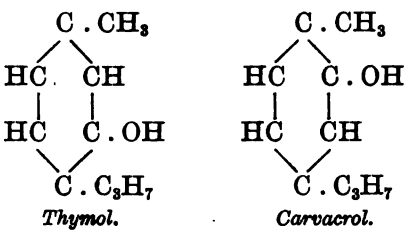
Apiol. *Isoapiol.*

where the numbers refer to the relative position of the radicles in the benzene nucleus. Here the C_3H_5 is the allyl group. The propenyl-apiols are of the same constitution, except that the C_3H_5 group represents the propenyl radicle in each case.

Phenols with Ten Carbon Atoms.

Methyl-propyl-phenol, $C_{10}H_{13}OH$.—Of the twenty possible isomeric forms of this phenol, only two are of common occurrence in essential oils. These are *thymol* and *carvacrol*. Thymol exists in various oils, notably in that of thyme. To obtain it in a fairly pure state, the oil can be shaken with a solution of caustic potash ; the aqueous layer, after separation, is treated with excess of hydrochloric acid, which precipitates the free phenol. It can also be prepared artificially from nitrocumic aldehyde. Thymol forms large, colourless crystals, melting at 44°, and boiling at 230°. It has an odour

resembling thyme, and is a very strong antiseptic. On distillation with phosphorus pentasulphide it yields cymene. Carvacrol occurs in a number of oils of the thyme family, especially in certain origanum oils and can be prepared artificially by heating carvone, an isomeric ketone, with phosphoric acid, or by heating camphor with iodine. It is a thick oil, solidifying at 0°, and distilling at 236°. The constitutions of thymol and carvacrol are :—



Thymol. *Carvacrol.*

They are both methyl-isopropyl phenols.

Alcohols.

A number of the aromatic alcohols occur in small quantities in a few oils, but the two following are the most common, occurring chiefly in some of the aromatic balsams :—

Benzyl alcohol, $C_6H_5 . CH_2OH$, is the simplest alcohol of the benzene series. It is a colourless liquid, of aromatic odour, occurring in the form of esters, chiefly in the balsams of Peru and Tolu and storax and in oil of jasmin and similar oils. It can also be obtained artificially by several methods, such as the reduction of benzaldehyde. It boils at 206°, and has a specific gravity about 1·055 at 10°. It is only slightly soluble in water, but readily so in alcohol and ether. Amongst the more important of its esters are benzyl benzoate, a crystalline compound melting at 21°, and benzyl cinnamate, melting at 39°. Both are aromatic bodies. Oxidation of benzyl alcohol gives rise to benzaldehyde and benzoic acid.

Styryl alcohol, $C_6H_5(CH : CH . CH_2OH)$, also known as

styrol or cinnamic alcohol, is γ-phenyl-allyl-alcohol. It exists as styracine, or cinnamyl cinnamate, $C_8H_7 . CO_2 . C_9H_9$, in storax. This body melts at 44°, and when boiled with alkalies yields the free alcohol and alkaline cinnamate. The alcohol is a crystalline solid, melting at 33° and boiling at 250°. It possesses a hyacinth-like odour.

Aldehydes.

These bodies are of more frequent occurrence than their corresponding alcohols. The more important of them are benzaldehyde, salicylic aldehyde, anisic aldehyde, cinnamic aldehyde, and cumic aldehyde.

Benzaldehyde, C_6H_5COH, is the main constituent of oil of bitter almonds and other oils of the same family. It can be formed in various ways, including the oxidation of benzyl alcohol, or, as is usually done, by acting on benzal chloride, $C_6H_5CHCl_2$, with sulphuric acid or with milk of lime, or by heating benzyl chloride, $C_6H_5CH_2Cl$, with water and lead nitrate. Artificial benzaldehyde is manufactured and sold largely as "artificial oil of almonds". It is almost identical with the natural oil, but possesses a rather harsher odour, probably due to the presence of traces of impurities, which generally consist of chlorinated compounds. A very pure variety, however, is now produced, which is free from these impurities. The natural benzaldehyde results from the decomposition of a glucoside, amygdalin, under the influence of the ferment emulsin in the presence of water (*vide* oil of bitter almonds). Benzaldehyde is a colourless liquid, of strong almond odour, of high refractive power, boiling at 179°. Its specific gravity is 1·050 at 15°. It is somewhat soluble in water, and freely so in alcohol and ether. It combines to form a crystalline compound with alkaline bisulphites, and, generally, exhibits all the usual properties of an aldehyde. It is easily oxidised by exposure to the air to benzoic acid.

Salicylic aldehyde, $C_6H_4(OH)(CHO)$.—This body is an oily liquid of aromatic odour, occurring in the oils of several varieties of *Spiræa*. It can also be formed artificially by the oxidation of its alcohol saligenin, or by the action of chloroform and caustic potash on phenol. It is an oil of specific gravity 1·172 at 15°, solidifying at − 20° and boiling at 196°. It is easily reduced by sodium to its alcohol saligenin, or oxidised to salicylic acid.

Anisic aldehyde, $C_6H_4(OCH_3)(CHO)$, exists in minute quantities in oils such as aniseed and fennel. Commercially, it is sold as "aubepine" or artificial hawthorn (*q.v.*). It is a colourless liquid of specific gravity 1·123 at 15°, boiling at 248°. It is prepared by the oxidation of anethol.

Cinnamic aldehyde, $C_6H_5(CH : CH . COH)$, is the chief ingredient of oils of cassia and cinnamon. It is prepared artificially in large quantities by the action of caustic soda on a mixture of benzaldehyde and acetic aldehyde, according to the equation—

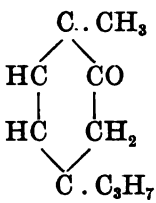
$$C_6H_5 . COH + CH_3 . COH = C_6H_5 . CH : CH . COH + H_2O.$$

The natural oils containing cinnamic aldehyde are, however, much finer in odour than the artificial product. Cinnamic aldehyde is a colourless oil, slightly heavier than water, boiling at 247°. It combines with alkaline bisulphites to yield a crystalline compound, and possesses all the usual properties of an aldehyde. It is easily oxidised to cinnamic acid.

Cumic aldehyde, $C_6H_4(C_3H_7)(CHO)$, or cuminol, is *para*-isopropyl-benzaldehyde. It is a constituent of several essential oils, notably Roman caraway oil. It is an aromatic oil, of specific gravity ·973, boiling at 235°. It forms a crystalline compound with sodium bisulphite, by means of which it can be separated in a state of purity.

KETONES.

The only ketone belonging to this series which occurs to any great extent in essential oils is *carvone* $C_{10}H_{14}O$ (also known as carvol). This body is the important constituent of oils of caraway and dill, in which it occurs in its dextro-rotary form. Laevo-carvone occurs in Kuromoji oil. It is isomeric with carvacrol, into which it is easily changed by the action of caustic alkali. Its constitution is :—



It is a colourless oil boiling at 225°. It is optically active, existing in both the *dextro-* and the *laevo-*rotary forms. The optical activity is usually given as 62°, but the purest specimen from oil of caraway examined by the author had a rotation of + 58·6°, and a specific gravity ·9619. Inactive carvone can be obtained by mixing equal quantities of the optically active isomers. Carvone yields all the usual ketonic compounds, such as the crystalline oxime and phenylhydrazone. The former compound is interesting on account of the fact that it is identical with nitrosolimonene (*vide* limonene). Carvone also forms a crystalline compound with sulphuretted hydrogen $C_{10}H_{14}(OH)(SH)$. This results by passing the gas through an alcoholic solution of caraway oil saturated with ammonia gas. The resulting crystals can be purified by recrystallisation, and decomposed by alcoholic potash, when nearly pure carvone results. The following table gives the optical rotations of the purest specimens of dextro- and laevo-carvone derivatives that have been prepared.

	Derivatives of	
	Dextro-carvone.	*Laevo-carvone.*
Carvone	+ 62°	− 62°.
Carvone sulphydrate . .	+ 5·53°	− 5·55°.
Carvoxime	+ 39·71°	− 39·34°.
Benzoyl carvoxime . . .	+ 26·47°	− 26·97°.
Benzoyl hydrochlor-carvoxime .	− 10·58°	+ 9·92°.

ACIDS.

The chief of the aromatic acids found in essential oils are benzoic, salicylic and cinnamic acids. These usually exist in the form of esters, the compounds with alcoholic radicles already referred to; occasionally, however, they are found in the free state.

Benzoic acid, C_6H_5COOH, is found to a large extent in the free state in various resins, and as benzyl benzoate, $C_6H_5CH_2 . CO_2 . C_6H_5$, in various essential oils. It also results from the oxidation of benzyl alcohol and benzaldehyde, and can also be prepared by numerous synthetic reactions. It forms white, shining leaflets, melting at 120°. It is readily volatile, either alone or with steam. It is but slightly soluble in water. Amongst its more important esters are methyl benzoate, $CH_3 . CO_2 . C_6H_5$, a liquid boiling at 199°; ethyl benzoate, $C_2H_5 . CO_2 . C_6H_5$, boiling at 213°; and benzyl benzoate, $C_7H_7 . CO_2 . C_6H_5$, melting at 21°.

Salicylic acid, $C_6H_4(OH)(COOH)$, is found naturally, chiefly as methyl salicylate, which forms almost the whole of oils of wintergreen and sweet birch. Salicylic acid itself is *ortho*-oxybenzoic acid, and when pure forms crystalline prisms, melting at 155°. It is slightly soluble in cold water, but easily so in most organic solvents. The pure acid may be obtained by boiling the natural oil in which it occurs, with alcoholic solution of potash, and decomposing the potassium salt with hydrochloric acid. After purification, the acid is found to be almost entirely free from foreign bodies. It can be obtained by numerous artificial methods, the chief

of which is that patented by Kolbe, or some modification of it, the patent having now expired. This consists of heating sodium phenol in a current of carbonic acid gas at 180° to 220°, when di-sodium salicylate results.

$$2C_6H_5ONa + CO_2 = C_6H_4(ONa)(CO_2Na) + C_6H_5OH.$$

The salicylic acid, liberated from this salt by means of acids, usually contains a little *para*-oxybenzoic acid, and, although modern methods of preparation and purification largely overcome this objection, the natural acid is always preferred to the artificial, and commands a higher price. The most important ester of this acid is methyl salicylate above mentioned. This body, $CH_3.CO_2(OH)C_6H_4$, is an agreeably smelling liquid, boiling at about 226°, of specific gravity about 1·20 at 15°. The oils of wintergreen and birch consist almost entirely of this body; so that methyl salicylate, obtained by passing a current of hydrochloric acid gas into a solution of salicylic acid in methyl alcohol, is now largely sold as artificial oil of wintergreen. An aqueous solution of sodium salicylate readily dissolves most oxygenated constituents of essential oils.

Cinnamic acid, $C_6H_5.CH:CH.CO_2H$, exists free in various resins, and to a certain extent in some essential oils. It can be prepared by numerous synthetic reactions, and is now of great importance, on account of its value in the synthesis of indigo. A useful method of obtaining the acid is to boil 3 parts of benzaldehyde with 3 parts of sodium acetate and 10 parts of acetic anhydride. Water is then added, the acid dissolved in alkali, and finally precipitated with HCl and recrystallised. Pure cinnamic acid crystallises in fine needles, melting at 133°. Styracine, the cinnamic ester of cinnamyl alcohol, has already been mentioned.

V. ALIPHATIC COMPOUNDS.

Apart from the open-chain compounds, already described under the geraniol and citronellol group, there exist in

essential oils a few bodies belonging to the open-chain or aliphatic series. The most common of these are the alcohols, aldehydes and acids belonging to the ethyl alcohol and acetic acid series. They usually exist either as the free alcohols and aldehydes, or as combinations of the alcohols and acids, as esters. For the purpose in view, the constitution and general properties of the most important of these will suffice.

Alcohols.

Methyl alcohol, $CH_3.OH$; liquid boiling at 66°, specific gravity, ·796 at 20°, soluble in water in all proportions. It exists in the free state in traces in oil of cloves; largely in the form of esters (*e.g.* with salicylic acid).

Ethyl alcohol, $C_2H_5.OH$; liquid boiling at 78°, of specific gravity ·8062 at 0°, soluble in water in all proportions. It exists in small quantities in the free state in several essential oils, and also as esters.

Propyl alcohol, $CH_3.CH_2.CH_2OH$; liquid boiling at 97°, of specific gravity ·8044 at 20°.

Isopropyl alcohol, $(CH_3)_2CH.OH$; an isomer of the last described body, boiling at 83°, of specific gravity ·7887 at 20°.

Butyl alcohol, $CH_3.CH_2.CH_2.CH_2.OH$; liquid boiling at 117°, of specific gravity ·8099 at 20°.

Isobutyl alcohol, $(CH_3)_2.CH.CH_2OH$; liquid boiling at 108°, of specific gravity ·8020 at 20°.

Isoamyl alcohol (isobutyl carbinol), $(CH_3)_2CH.CH_2CH_2OH$; liquid boiling at 131°, of specific gravity ·8104 at 20°.

Hexyl alcohol, $C_6H_{13}.OH$; liquid boiling at 157°, of specific gravity ·819 at 23°.

Octyl alcohol, $C_8H_{17}OH$; liquid boiling at 191°, of specific gravity ·830 at 16°.

Acids.

Acetic acid, CH_3COOH; acid corresponding to ethyl alcohol, from which it can be obtained by oxidation; occurs largely in the form of esters, such as geranyl acetate, bornyl acetate, menthyl acetate, etc., in many essential oils; a crystalline solid, melting at 16·7° when absolutely pure, but liquid if it contains more than traces of water; boils at 118°, specific gravity, 1·0514 at 20°.

Propionic acid, $C_2H_5.COOH$; liquid boiling at 140°, of specific gravity ·992.

Butyric acid, $CH_3.CH_2.CH_2.COOH$; liquid boiling at 163°, of specific gravity ·9587 at 20°; found chiefly as hexyl and octyl esters.

Isobutyric acid, $(CH_3)_2CH.COOH$; liquid boiling at 155°, of specific gravity ·949 at 20°; found both in the free state and as esters.

Valeric acids, $C_5H_{10}O_2$.—Normal valeric acid does not appear to be found in any essential oils. Isovaleric acid $(CH_3)_2CH.CH_2.COOH$, is found; it is a liquid boiling at 174°, of specific gravity ·947. Another isomer, also found in essential oils, is methyl-ethyl-acetic acid, $(C_2H_5)(CH_3).CH.COOH$. This is an optically active liquid, boiling at 175°, of specific gravity ·941 at 21°.

Caproic acid, $C_5H_{11}COOH$; liquid boiling at 205°, solidifying at − 2°, specific gravity, ·928 at 20°. (The above-described acids are mono-basic, belonging to the acetic series.)

Tiglic and angelic acids, $C_5H_8O_2$.—These two acids are geometrical isomerides. They are unsaturated acids, belonging to the acrylic series. Tiglic acid forms crystals melting at 64·5°; angelic acid melts at 45°. The constitutions of these bodies are:—

$CH_3 . CH$	$CH_3 . CH$
‖	‖
$CH_3 . C . COOH$	$COOH . C . CH_3$
Angelic acid.	*Tiglic acid.*

These two acids occur chiefly as esters in Roman chamomile oil. Tiglic acid is also found as geranyl tiglate in geranium oil.

Hydrocyanic acid, HCN.—This very poisonous acid occurs in bitter almond oil, and other oils of the same family, but is frequently removed from the oil before it is used. When pure, hydrocyanic or prussic acid is a mobile liquid of specific gravity ·697 at 18°, and boiling at 26·5°.

Aldehydes.

Acetaldehyde, $CH_3 . COH$, is the aldehyde corresponding to ethyl alcohol and acetic acid. It is a liquid of peculiar odour, boiling at 21°, of specific gravity ·8009 at 0°. It has been found in one or two oils.

Valeric aldehyde, $(CH_3)(CH_2)_3 . CHO$; liquid boiling at 102°.

Isovaleric aldehyde, $(CH_3)_2CH . CH_2 . CHO$; liquid boiling at 92°.

Sulphur Compounds.

Vinyl sulphide, $(C_2H_3)_2S$, is a constituent of oil of *Allium ursinum*. It is a liquid of noxious odour, boiling at 101°, of specific gravity ·9125.

Allyl sulphide, $(C_3H_5)_2S$, is a constituent of oil of garlic, and occurs in many oils belonging to the *Cruciferæ*. It is a liquid of very unpleasant odour, boiling at 140°.

Allyl thiocyanate, $C_3H_5 . NSC$, is the principal constituent of ordinary mustard oil. It results from the decomposition of the glucoside, potassium myronate, which breaks up under the influence of the ferment myrosin in the presence of moisture, as follows:—

$$C_{10}H_{18}KNO_{10}S_2 = C_6H_{12}O_6 + KHSO_4 + C_3H_5 . NSC.$$

Potassium myronate. *Glucose.* *Allyl thiocyanate.*

It can be obtained artificially by distilling allyl iodide or bromide with alcoholic potassium thiocyanate. Such a product is generally sold as artificial mustard oil, and it has largely replaced the natural oil. It is a foul-smelling liquid, boiling at 151°, of specific gravity 1·017 at 10°.

Other Bodies.

Methyl nonyl ketone, $CH_3 . CO . C_9H_{19}$, is a ketone belonging to the fatty series which is found to a small extent in essential oils. It occurs in oil of rue, and is a liquid of strong odour, boiling at 225°. If cooled it solidifies, and then melts at 13°. Several allied ketones are also found in a few essential oils.

Paraffins.—A number of solid hydrocarbons have been found in several oils, such as oil of roses, which probably are members of the paraffin series of the general formula C_nH_{2n+2}, but at present little is known definitely of the exact chemical relationships of these bodies.

CHAPTER III.

THE PREPARATION OF ESSENTIAL OILS.

THE methods used for obtaining essential oils from the plants yielding them vary greatly, not only in principle, but also in detail. Indeed, in many cases where the principles underlying the various processes are identical, the actual details are governed by so many circumstances, that only an intimate knowledge of the chemistry of the bodies in question, coupled with a liberal practical experience, will ensure the attainment of the best results. The present chapter is devoted to a brief outline of the most important processes in general use, without devoting too much space to details, which, treated in a text-book, could not yield the practical man nearly so much information as could be obtained during a short stay in a factory. Generally speaking, the processes used for obtaining essential oils may be grouped under the three headings—Expression, Distillation, and Extraction with a solvent (the latter including the various absorption processes).

EXPRESSION.

This process is only of value in those cases where the substances operated upon contain a considerable amount of oil, and are of a certain degree of softness.

In general, the principle of the process is as follows: the substance yielding the oil (the peel of the orange, lemon, bergamot, etc.), freed as much as possible from all adhering substances, such as the soft endocarp, is placed in a cloth

and subjected to great pressure. The form of the press, and the nature of the power used, will vary according to the quantity operated upon, etc. The liquid expressed from the substance is usually an opaque milky fluid, which consists of the oil, water and various solids, either dissolved in the water or held in suspension. The liquid, on standing in tall narrow vessels for a few days, separates into two layers, the oil on top and the watery fluid below. This latter generally shows division into two layers itself, the bottom one consisting of a deposit of the various albuminous and cellular substances which were held in suspension in the liquid. The crude oil is separated in the ordinary way by any mechanical appliance which will allow the liquids to be run off as in a separatory funnel. Such, for example, is a bottle with lateral taps, by which the water is first run off through a lower tap; the oil can be run off almost completely through an upper one. The oil, however, is always turbid, and requires purification, either by distillation or filtration. In the special cases mentioned distillation impairs the quality of the oil, so that filtration is resorted to. As this operation requires some time, it is of the greatest importance to exclude, as far as possible, any excess of air. This indeed is usually necessary when dealing with essential oils, for most of them are easily oxidised, and care should be taken to prevent the action of the air; and as this is accelerated by heat and light, cool dark places are usually the most suitable for storing them in. The following diagram shows the principle of a useful and simple filter which can be used for many oils. It possesses the advantage of excluding all air from acting on the oil during filtration, except that contained in the apparatus when the operation is started.

Here F is the top of a glass receiving bottle, closed by a tightly fitting cork with two holes in it. The top rim of

the glass funnel, T, is ground smooth and covered with a smooth wooden plate, D, with an india-rubber ring on its lower side, and pierced by a hole in the centre. Through this hole is placed a bent glass tube, which is fitted tight into the hole by means of a rubber cork, and securely connected with the rubber tube, K. This terminates in another bent glass tube which, with the nose of the funnel, pierces the cork of the receiver. When the filter paper is placed in the funnel and this is filled with the oil, the lid is fixed on and need not be removed, except to fill up the

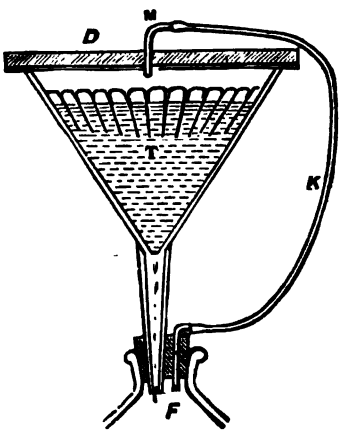


FIG. 2.

funnel again, until the receiver is full. By this means the air of the receiver is gradually driven into the funnel to take the place of the oil, and so contact with the outside air is entirely avoided.

As a matter of fact, the use of an actual press is but rarely employed in the preparation of the oils above mentioned (lemon, orange, etc.). The following processes, in which very little pressure is used, are largely employed in the preparation of this group of oils. In Sicily and the south of Italy the *éponge* or sponge method is very largely employed.

This has been described by various writers, and probably the following description by Mr. Arthur Barrett (*Year Book of Pharmacy*, 1892, p. 505) is as accurate as any. He says: "The principle on which the extraction of the essence is carried out may be illustrated in this way. If you hold a piece of lemon peel up to the light, and turn it inside out, a fine shower of mist will be seen to be forcibly ejected. This is not all oil, but a mixture of oil and water. Most people are unpleasantly acquainted with this phenomenon, though many may not have actually seen it, for in peeling a lemon or orange with the fingers a little of the oil is often ejected into the eye, causing a considerable amount of pain. By turning the lemon peel inside out almost the whole of the essence is removed from the peel, for each little globule of oil appears to be surrounded by water, and the liquid which remains adherent to the peel consists principally of water. As it is impossible to turn every piece of peel actually inside out, the following method is adopted. One man takes a lemon in his hand, and with three rapid strokes with a large knife cuts off nearly all the peel in three slices. The central portion which is left consists of most of the pulp with a little of the peel—top and bottom. This is simply pressed for making lemon juice. The slices pass to a second workman, who sits on a low chair with a common quality bath sponge, worth about sixpence, in one hand. With the other he presses the slice of peel against the sponge, pressing the edges of the peel only with his fingers, the object being to press the convex piece of lemon peel as nearly flat as possible. The amount of pressure used is very slight, and at first sight it seems incredible that the oil globules can have been broken; but, if you try the experiment of turning this exhausted peel inside out, nothing more can be extracted. The sponge is periodically squeezed. One man working in this way can extract 1½ lb. (English)

essence of lemon per day. To ensure the cells being fully charged with moisture it is usual to allow the lemons to stand in water for a short time; and I myself propose washing the lemons in a stream of running water."

The *écuelle* process, which is employed in the north of Italy and the south of France, depends on the preliminary breaking of the oil globules by means of spikes or knives, and varies in detail, according to the quantity to be operated upon. A simple *écuelle* is a saucer-shaped vessel, about 8 in. to 10 in. in diameter, usually made of copper, tinned inside, and covered inside with short spikes, about $\frac{1}{4}$ in. to $\frac{1}{3}$ in. long. In the bottom of the saucer is a hole about $\frac{1}{2}$ to $\frac{1}{3}$ in. in diameter, leading to a hollow tube about 4 in. or 5 in. long. A fruit is placed in the vessel, and, by means of a rapid rotary motion, causes the oil cells to be broken by means of the spikes. The escaping oil flows into the hollow tube, which is periodically emptied.

In both these cases the peel is frequently treated, after all the oil possible has been obtained, either by soaking in warm water or by distillation, to obtain the remainder of the oil, which is of an inferior quality, as distillation impairs the value of these oils.

An apparatus, known as the thermopneumatic extractor, has been invented by Montfalcone for the extraction of all varieties of *citrus* oils. The inventor claims that a far higher yield of oil of equal quality is obtained by the use of his apparatus, which is described as follows:—

1 is a hollow cylinder of sheet iron, the interior surface of which is studded with a large number of metallic knife-points. This cylinder revolves on two axles, attached to it at diagonally opposite points. Its capacity is such that, when charged, it is capable of holding 1200 or 1500 lemons. The cylinder having been properly charged, say with the above-mentioned number of lemons, together with a small

quantity of water, it is set in motion by aid of the shafting and pulleys, driven by the small steam-engine. The fruits are thereby made to come in contact with the metallic lancets, and their whole surface gradually becomes punctured sufficiently to cut or rupture the cells containing the essential oil, which escapes. The cylinder, 1, has double walls, the space between them being intended for the circulation of a current of steam, which is admitted to heat the water and to facilitate the extraction of the oil, while, at the same

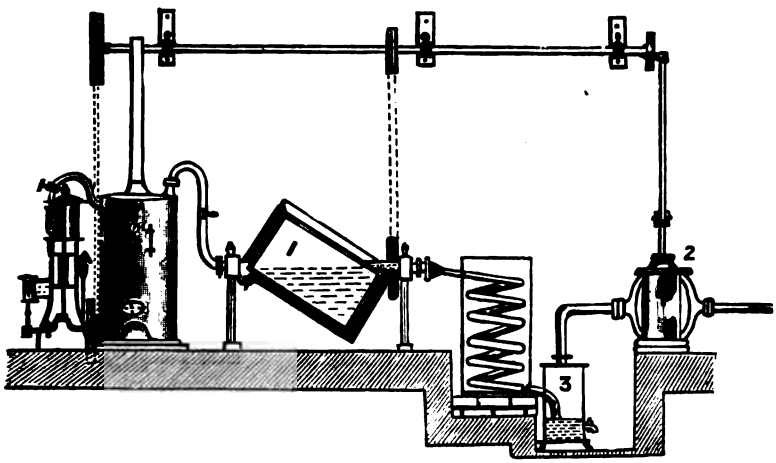


FIG. 3.

time, the vapours are rarefied or aspirated by the vacuum-pump, 2. The axles of the cylinder on both sides are hollow: that on the side looking towards the engine is embedded in such a manner that steam from the boiler may be admitted at will, either into the double walls of the cylinder or into the interior of the cylinder itself; while the hollow passage in the other axle communicates with a condensing-worm the outlet of which descends into a cylindrical vessel, 3, intended to receive the condensed products, consisting of water and essential oil. When the apparatus is first set in

motion, the pump begins to produce a vacuum during the first revolutions of the cylinder. Steam being now cautiously admitted into the double walls of the cylinder, the water is raised to boiling at a comparatively low temperature, and the vapours charged with the essential oil rapidly pass over into the receptacle. With a two-horse-power engine and a boiler designed for a five-horse-power engine, five such machines may be driven at once, and the operation, including the time required for charging and emptying, is completed in three-quarters of an hour.

Schimmel (*Report*, April, 1896) says that lemon oil is in general manufactured in three ways :—

"1. The *Spugna* process. This is the traditional operation with sponges, as described by Prof. Flückiger in his well-known sketch, 'Easter Vacation in the South' (*Arch. d. Pharm.*, vol. iii., xxvii., p. 1065).

"2. The *Scorzetta* process. The fruits are cut into two halves, the pulp is removed with a kind of spoon, and all the parts of the peel are then pressed against a sponge by constantly turning it in the palm of the hand. This method has the advantage that the peels remain unbroken, and retain their original appearance. After they have been deprived of the oil, they are salted, and then exported under the name 'Salato'. The pulp also remains unimpaired, so that it yields its full supply of lemon juice. After having passed twice through the pressers it is used for feeding cattle.

"3. The *Machina* process. A number of contrivances have been tried for obtaining the essential oil of agrumini fruits by other less empirical and more economical methods. More recently a machine, which has a rather complicated construction but works very well, has come into use in Nizza di Sicilia, Mascali and Tremestieri. The product obtained by this process, however, is said to be less profitable, because both the quantity obtained and the quality of

the oil leave much to be desired. It must remain to more extended experience to demonstrate whether this machine will prove a success, or whether it will fall into oblivion, like most of its predecessors."

Distillation.

The majority of essential oils are obtained by a process of distillation, but the question, when treated as fully as it deserves, becomes so largely an engineering matter that no attempt is here made to deal with the *technique* of the various processes. A few words on the principles underlying the general methods adopted will amply suffice for the purpose in view. In the first place, it is to be noted that great attention has to be paid to the properties of the oils, and of their individual constituents, in deciding what treatment is most advantageous. Many compounds are decomposed by distillation, notably certain esters; others are modified by heat to such an extent, that distillation materially impairs the odour of the oil. Certain oils, obtained by other processes, are submitted to the process of distillation, or rectification, as it is then termed, and often the quality is by no means improved. This is the case with oil of bergamot, in which part of the linalyl acetate is decomposed into its constituents on distillation, and an inferior oil results.

The early process used in civilised countries, and which is still used largely by those which are less civilised, was distillation by means of an open fire. There the portion of the plant which yields the volatile oil is prepared in the most advantageous manner, and introduced into an ordinary still with the requisite quantity of water. When the fire is applied the water boils, and the steam carries over with it the essential oil of the plant. The steam carrying the oil, either in vapour itself or mechanically suspended, is condensed, and the resulting oil separated from the water in

any of the usual ways. Two disadvantages are very clearly indicated here. Firstly, the plant itself may very easily be burnt, with the result that the oil has a disagreeable empyreumatic odour; secondly, a very careful adjustment of the amount of water is necessary. Too small a quantity increases the risk of burning the plant substance, whilst too much water results in a very large distillate, and, as all oils are slightly soluble in water, a considerable quantity is lost, or at best is only recovered in the form of an aromatic water. As an example of the effects of heat, when a direct-heat still is used, the very high specific gravity and inferior quality of the native distilled sandal-wood oil in India, as compared with that distilled in England, may be quoted.

To obviate this disadvantage, the simplest modification is that used to a large extent in distilleries which turn out some of the best oil produced. This consists in suspending the plant substance in copper cages, which do not quite touch the bottom of the still. The water is run in, to the proper quantity, and when heat is applied the water boils without any danger of the plant substance being burnt. Or a false perforated bottom may be used, upon which the plants are placed. Some such modification of this is used in the distillation of various flowers in England, and, as several English oils are undoubtedly the finest the world produces, it is clear that the process used cannot be other than a good one. In such a case the body of the still should be very shallow, as compared with its width, in order to allow the oil to distil over as rapidly as possible, as otherwise the oil first carried up by the steam from the bottom of the mass of flowers would be deposited in the cooler top portion of the still, and remain there until again taken up by the rising steam. This means a longer exposure to heat, which is never advantageous to any essential oil, and is certainly detrimental to one with a delicate odour.

A convenient method of preventing the plant from being injured by proximity to the fire is shown in the following diagram:—

Here the plant substance is placed in the vessel, A, which has an opening, covered with wire gauze, into the steam generator, B. When the water is boiled over an open fire, the steam passes through this opening, and permeates the plant mass, carrying over the essential oil through the outlet, C, into the condensing tube.

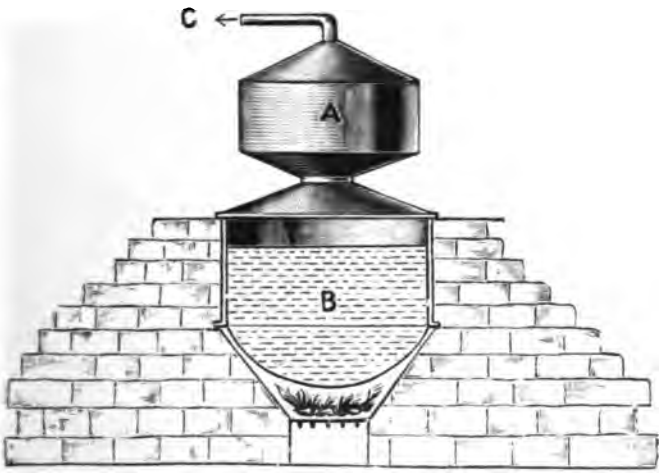


FIG. 4.

In general, however, the process of steam distillation, in which the steam is generated in a boiler, and let, by means of a pipe, into the mass of plant substance in the still, possesses many advantages. The plant is never exposed to the danger of burning, and the minimum quantity of water is collected with the oil. To decrease the quantity of water to the minimum, it is of great advantage to maintain the plants at a high temperature, independently of the steam used for distillation. This is best effected by lining the still with a coil of pipes, through which high pressure steam passes.

By this means the mass is heated without any danger of burning, and without adding any water to it. It is then in a good condition for the steam to rapidly carry over the oil, and, in addition to the use of less water for distillation, the time taken by the process is materially shortened.

The following description of a still used by Schimmel & Co. will illustrate the use of steam, both for distillation and for the purpose of heating, as described above. The still itself is a tall, conical body, A, with a perforated false bottom, about 8 in. from its true bottom. Upon this the

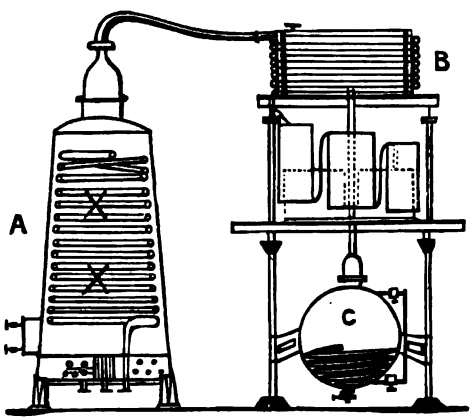


FIG. 5.

plants are placed, and immediately underneath steam enters by a pipe, which is coiled round and perforated under the false bottom. A coil of pipes, XX, having no opening inside the still, lines the whole of the interior, and through this steam is passed, which is kept at any required pressure and temperature. In the middle of the still mechanical stirrers are fixed, which materially increase the rate of distillation by continually turning over the whole mass. The steam from the bottom perforated coil traverses the whole mass, and carries over the essential oil through the outlet at the

top of the still, and is condensed in the ordinary way in the condenser B, through which it passes to a series of separators to the collecting flask C.

A further advantage is obtained especially in cases where the odour of the oil is very delicate by conducting the operation under a greatly reduced pressure. Not only can the distillation be carried on at a lower temperature, but it is much more rapid, and the quantity of water condensed is not excessive. The only disadvantage arising is the fact that a certain quantity of the oil may be lost in the vapour not condensed in the receiver, which is carried away by the exhaust pump. However in practice this is not a very serious matter. Distillation under greatly reduced pressure is largely used in the preparation of "terpeneless" oils.

Such are the principles of the processes generally employed in the distillation of essential oils. Some details will be given under special oils when treated systematically, when points of interest in connection with their preparation arise.

For a useful historical account of this subject the reader should consult the work published by Messrs. Schimmel & Co. edited by Gildemeister and Hoffmann.

Extraction.

All those processes by which the volatile oil is obtained by subjecting the plant substance to contact with some substance which dissolves the oil, and from which it may be afterwards recovered, may be conveniently grouped under the general heading of "Extraction". The more important of these are the following: (1) Extraction by means of a volatile solvent, which can afterwards be distilled off at a low temperature from the oil; (2) Extraction by means of a non-volatile solvent, from which the oil is recovered by dissolving it out again by means of a fresh solvent which is volatile, and does not dissolve the original solvent. The

well-known process used largely in France, and termed "enfleurage," may be taken as a type of this process; (3) Extraction by means of a current of air.

Extraction with a Volatile Solvent.—The essential oils are in general freely soluble in many organic liquids, such as ether, petroleum ether, chloroform, carbon disulphide, methyl chloride, etc. The process consists in extracting the oil by means of one of these solvents and afterwards distilling off the solvent, leaving the oil behind. There are a number of conditions essential to the successful working of this process. The solvent frequently dissolves much resin, colouring matter, etc., so that it is impossible to use the process of extraction with many plants without a further process of rectification. Consequently it is necessary to ensure that the solvent and the plant substance are so adapted that practically nothing but the oil is dissolved. In certain cases where the plant is treated in an out-of-the-way place, and distilling apparatus cannot be used, the plant is extracted with the solvent, and a mixture of oil, colouring matter and resin is obtained. On submitting this when it arrives at the distillery to steam distillation, the oil is obtained in a fairly pure condition. Again, it is necessary that the solvent should have a low boiling point, so that it can be distilled without unduly heating the oil, and without any of the oil being carried over with it. The following solvents are applicable to numerous cases :—

	Specific Gravity.	*Boiling Point.*
Carbon bisulphide CS_2 .	1·297 at 0°	47° C.
Alcohol (ethyl) C_2H_5OH .	·789 at 20°	78° C.
Alcohol (methyl) CH_3OH	·796 at 20°	66° C.
Methyl chloride CH_3Cl .	(gas at ordinary temperatures)	− 24° C.
Chloroform $CHCl_3$ . .	1·5008 at 15°	61° C.
Acetone $CO.(CH_3)_2$.	·792 at 20°	56·5° C.
Petroleum ether . .	·626 to ·700	
Benzene C_6H_6 . . .	·899 at 0°	80·5° C.
Ether $(C_2H_5)_2O$ . .	·736 at 0°	35° C.

The simplest process of extraction is merely an adaptation of the ordinary method of percolation, or, with a view to economise the solvent used, an apparatus on the principle of the ordinary Soxhlet tube is used. The chief point to be noted is the arrangement of the apparatus so that the minimum quantity of the volatile solvent shall be lost. Various patents have been taken out in respect of extraction processes, amongst them being several involving the use of the very volatile solvent methyl chloride. One of these is well illustrated in the *Pharmaceutical Journal* [3], xiv., p. 44. Most of these are very complicated as regards the arrangement of vessels and pumps, but a simple process, in which methyl chloride is used, is described by Blogg in his evidence given before the Royal Commission of Inquiry into the vegetable products of Victoria. A jacketed vacuum still, fitted with the pump and condenser, a closed macerating vessel and a receiver are all the apparatus necessary. The fresh flowers, for it is nearly always fresh flowers that are treated in this way, are placed in the macerating vessel, which is filled up with pure methyl chloride and kept tightly fastened for a quarter of an hour. The liquid is then rapidly transferred to the vacuum pan, this is warmed and the exhaust pump is started. The solvent is rapidly evaporated, leaving the extracted oil, etc., in the pan. Great care must be exercised to see that the methyl chloride is as pure as possible. Much of the commercial product is manufactured from the trimethylamine obtained by destructively distilling the residues obtained from crystallisation of beet sugar. To purify it, it is best to pass it through hydrochloric acid, and then to dry it with calcium chloride. It is then compressed into iron cylinders, when it forms a mobile liquid. To purify oils obtained by such processes it is necessary either to dissolve them out with alcohol from the wax, etc., which is extracted with them from the plants, or to purify them by a process of rectification

(distillation). Extraction with a solvent in the cold may be accelerated by fixing the vessel containing the solvent at a much higher level than the percolator. These are connected by a vertical pipe, the connections being made perfectly tight, with the result that the pressure of the liquid on the substance to be extracted is greatly increased, and the process is thereby much accelerated.

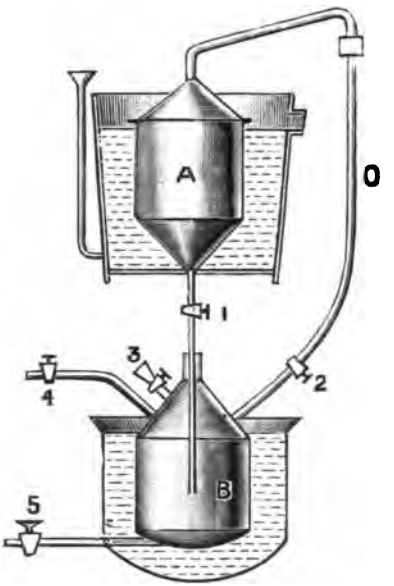


FIG. 6.

The above diagram represents a simple apparatus for extraction on the Soxhlet principle. The flowers to be extracted are placed in the vessel A, immersed in a tank of cold water, and the solvent is placed in the vessel B, immersed in a tank of warm water. When the connections have been made all the taps except 1 and 2 are closed, and the water in the tank surrounding B is heated sufficiently to make the solvent boil. This passes up the tube O and enters

the vessel A, where it condenses and penetrates through the mass of flowers, finding its way back to B through the vertical tube. The solvent is again evaporated, leaving the extracted oil in B, thus making the process continuous. When exhaustion is complete, taps 1 and 2 are turned off, and tap 4 is turned on. The solvent is then evaporated and passes through this tap to a condenser, and finally the residual oil is run off through the lowest tap. Any fresh supply of solvent necessary is poured into B through the funnel 3.

Extraction with a Non-Volatile Solvent.—The processes known as maceration and enfleurage are types of this method. The former is used in certain parts of France in the following manner. A quantity of a pure neutral fat such as olive oil or lard is placed in a pan heated by a water bath. The freshly gathered flowers are thrown in and left there twelve to forty-eight hours, as the case may be. The whole is frequently stirred. When the odour is entirely gone from the flowers, the fat is strained off into a fresh pan, and another lot of fresh flowers is thrown in. This operation is repeated a dozen or more times, until the pomade, as it is called, usually having a fine solid fat such as pure lard for its basis, is sufficiently strong. It is found that the odour is invariably the most delicate when the flowers have remained for the shortest time in contact with the fat. Various devices are employed in order to reduce the time of maceration, amongst which one deserves especial notice. This consists of a reservoir, containing the fat heated to about 65° or 70° C., from which it flows in a slow stream through the macerating chamber, a long tank in which wire cages of flowers are suspended in open compartments. Every now and then the basket nearest the oil reservoir is emptied and taken out, and all the other baskets moved on one compartment, a fresh basket of

flowers being added at the other end. A constant movement of the oil and the flowers in opposite directions is thus ensured, and the time of maceration is materially reduced.

The oily solution has then to be treated in order to obtain the perfume from it. If olive oil has been used, it is well shaken repeatedly with pure alcohol, which after a time dissolves out nearly all the volatile oil, from which it can either be separated by careful distillation, or it can be used directly as a perfume. If a solid fat such as lard has been used, it is necessary to cut it up into very small pieces, or mechanically divide it in some other way, in order to expose the largest possible surface to the action of the alcohol. The French process of enfleurage is used in those cases where the flowers possess so delicate an odour that the oil would be damaged by the application of heat. The process is tedious and expensive, and the yield from the flowers is always small. Hence the high price of perfumes obtained by this process. A series of rectangular wooden frames, about 2 ft. × 3 ft., with a square of strong glass fitting in their inner rims, known as "chassis," are laid one upon another to form a pile. On each is spread a very thin layer of pure neutral fat. About six to eight ounces are used for each frame. The fresh flowers are then spread upon these and allowed to remain for a period of from a half to three days. When the flowers have lost their odour, fresh ones are spread out in their place, until the fat acquires a very strong odour. *Chassis à huile* are frames provided with wire netting on which cotton or linen cloth soaked in olive oil is spread. The whole process, until the fat or oil is saturated with the odorous oil as far as is desired, takes two to three months. The fat is then removed from the glass, or the oil pressed from the cloths by a hydraulic press, and can either be used as *pomades*, or can be treated with alcohol to extract the perfume. Of late years very highly purified

hydrocarbon jellies have been used, to some extent, for enfleurage, with some success.

The process of absorption can be carried out more rapidly by arranging a series of *chassis* so that air can be drawn through the apparatus, to pass successively over all the plates. The flowers are then not placed on the fat at all, but in a separate vessel connected by a pipe to the box containing the *chassis*. Air is then drawn through the flowers, and over the layers of fat, which absorb practically the whole of the perfume, without ever coming into actual contact with the flowers. One great advantage of this process is that the fat is less liable to become rancid than it is when placed in contact with the fresh flowers. A current of carbonic acid gas is sometimes used, in order to prevent the possibility of oxidation by means of the air.

A current of hot air is sometimes used to extract the perfume from flowers which are not too delicate to stand the treatment. But as the hot air rapidly dries up the plant, and hinders it yielding up the remainder of its volatile oil, it is necessary to ensure the air being saturated with moisture before it reaches the flowers. This is best effected by allowing it first to pass through a series of wet sponges. The air, after passing over the flowers, passes through a flask containing carbon bisulphide, or some other solvent with a low boiling point, which absorbs the oil from the air, and from which it is easily recovered.

The following table, giving the average yield obtained from the most common of the essential oils, is based on the statements of Messrs. Schimmel & Co., Leipzig.

Plant.	Per cent.	Plant.	Per cent.
Ajowan (seed)	3 to 4	Eucalyptus oleosa	1·25
Allium (plant)	·007	— staigeriana	2.5 to 3·7
Angelica (fruit)	1 to 1·2	Fennel (fruit)	1 to 6
— (herb)	·02	Galbanum (resin)	14 to 22
Angostura (bark)	1·5	Geranium (herb)	·18
Anise fruit, Chili	1·9 to 2·6	Ginger (rhizome)	2 to 3
— — Italian	2·7 to 3·5	Hop (flowers)	·3 to 1
— — Mexican	1·9 to 2·1	Hyssop (herb)	·3 to ·9
— — Prussian	2·4	Jaborandi (leaves)	·4
— — Russian	2·4 to 3·2	Juniper (berry)	·6 to 1·5
— — Spanish	3	Lavender (flowers)	variable
— — Syrian	1·5 to 6	Lemon (peel)	variable
— — Thuringian	2·4	Linaloe (wood)	...
Arnica (flowers)	·04 to ·07	— Guiana	1
— (root)	·5 to 1	— Mexico	7 to 9
Asafœtida (resin)	3·3 to 3·7	Lovage (herb)	·1 to ·2
Bay (leaves)	2·3 to 2·5	— (fruit)	1 to 2
Bergamot (peel)	variable	— (root)	·3 to 1
Bitter almonds	·5 to 1	Mace (arillus)	4 to 15
Buchu (leaves)	1 to 2	Mandarin (peel)	variable
Calamus (herb)	·2	Marjoram (herb)	·3 to ·9
Camphor (leaves)	1·85	Matico (leaves)	1 to 3·5
— (wood)	4	— (leaves and flowers)	3·5 to 5·5
Canella (bark)	·7 to 1	Mignonette (flowers)	·002
Caraway (fruit)	3 to 7	Mint (*arvensis*)	·22
Cardamoms (fruit)	2 to 8	Mustard (seeds)	variable
Cascarilla (bark)	1·5 to 3	Neroli (flowers)	·1
Cassia (leaves)	·54	Nigella (seeds)	·5
— (buds)	1·9	Nutmeg (fruit)	8 to 15
— (flower stalks)	1·7	Onion (herb and bulb)	·004
— (bark)	1·2	Orange (peel)	variable
— (twigs)	·2	Origanum (herb)	2 to 3
Cedar (wood)	2·5 to 4·5	Parsley (fruit)	2 to 6
Celery (herb)	·1	Patchouli (leaves)	1·5 to 4
— (fruit)	2·5 to 3	Pennyroyal (leaves)	3
Chamomile (flowers)	...	Pepper (fruit)	1 to 2
— German	·1 to ·3	Peppermint (herb)	·1 to 1·5
— Roman	·8 to 1	Pine (needles)	·1 to ·8
Cinnamon (bark)	·5 to 1	Rose (flowers)	·02
— (leaves)	1·8	Sage (leaves)	1·5 to 2·5
Citron (peel)	variable	Sandalwood	1·6 to 5
Citronella (grass)	variable	Sassafras (root bark)	7 to 8
Clove (buds)	15 to 18	Savin (twigs)	4 to 5
Copaiba (balsam)	40 to 80	Spearmint (herb)	·3
Coriander (fruit)	·2 to 1	Spike (herb)	variable
Cubeb (fruit)	10 to 18	Staranise (fruit)	5
Culilaban (fruit)	3·5 to 4	Storax (balsam)	·4 to 1
Cumin (fruit)	2·5 to 4	Tansy (herb)	·1 to ·3
Damiana (leaves)	·9 to 1	Thuja (leaves)	·5
Dill (fruit)	2 to 4	Thyme (herb)	·3 to 2·6
Dittany (herb)	·7	Turpentine (French)	16
Eucalyptus (leaves)	...	Valerian (root)	·5 to 1
— amygdalina	3·3	Veti-vert (root)	·4 to ·9
— citriodora	1 to 4	Wintergreen (true)	·75
— dealbata	2·7	— (sweet birch)	·6
— globulus	·8 to 3	Wormseed (fruit)	1
— odorata	1·4	Ylang-Ylang (flowers)	very small

CHAPTER IV.

THE ANALYSIS OF ESSENTIAL OILS.

In general, the analysis of essential oils merely involves the application of the ordinary principles of analytical chemistry to this special group of bodies, which possess many features in common. Of course many special processes have to be used in certain cases, to which attention will be drawn where necessary. The present chapter will be devoted to the details of a few methods which are in very common use in the analysis of these bodies, and which are absolutely necessary in order to form an opinion on the purity of very many oils. Particular processes will be mentioned as required. These remarks may be prefaced by saying that the obtaining of the results of an analysis is not always as difficult a matter as the interpretation of the same when obtained.

Specific Gravity.

The first thing to be done in examining an essential oil is to determine its specific gravity. For this purpose hydrometers are useless. Approximate accuracy is useless in this work, and hydrometers are only capable of yielding approximate results. Besides, one frequently has far too little oil at one's disposal to use a hydrometer. For ordinary work a specific gravity bottle is generally used, holding either 25 or 50 c.c. There are two points to be noted in connection with this. The graduated bottles sent out by apparatus firms seldom contain the exact quantity they are supposed to do. It is therefore advisable to check the contents of the bottle, and to use

the necessary correction when calculating a specific gravity. Secondly, the counterpoise of a 50 c.c. bottle should be about 60 milligrammes less than its apparent weight when empty on account of the air contained in the bottle. A consideration of the laws of hydrostatic pressure will show that if this be not so the specific gravity as determined will be the ratio

$$\frac{\text{weight of oil} - \cdot 06 \text{ gramme}}{\text{weight of water} - \cdot 06 \text{ gramme}}$$

instead of the correct ratio

$$\frac{\text{weight of oil}}{\text{weight of water}}.$$

This correction of ·06 gramme is not absolutely accurate, but is sufficiently so for all practical purposes and may be omitted in most cases.

It is essential that great care should be taken that the temperature be accurately determined when taking the specific gravity. The bottle filled with oil takes some time to assume the exact temperature of the water in which it is immersed, especially if these differ much at first. Hence it is always advisable not to depend only on an observation of the temperature of the water, but to use a very small bulbed thermometer, with which the actual temperature of the oil itself in the bottle can be taken. Specific gravities are usually expressed as the ratio of the weight of a volume of the oil to that of an equal volume of water, both at 60° F., or approximately 15·5° C. This is written $\frac{d15{\cdot}5^{\circ}}{d15{\cdot}5^{\circ}}$. Any variation in temperature can thus easily be expressed. For example, the specific gravity of, say, otto of roses at 30°, as given in the British Pharmacopœia, is intended to be interpreted as $\frac{d30^{\circ}}{d15{\cdot}5^{\circ}}$, that is, with the water to which it is compared at 15·5°. Wherever the specific

gravity of an oil is referred to in this work, it is to be understood as referring to $\frac{d15{\cdot}5^{\circ}}{d15{\cdot}5^{\circ}}$, except when otherwise quoted.

Frequently one has less than 50, and sometimes even less than 10 c.c. of an oil at one's disposal. The specific gravity should then be determined in a Sprengel tube. The following diagram shows the most convenient form of tube for general use. With a very small knowledge of glass-blowing they can be made in five minutes out of a few inches of glass tubing. The only important point is to choose a piece of thick walled tubing, otherwise it is impossible to draw out satisfactory

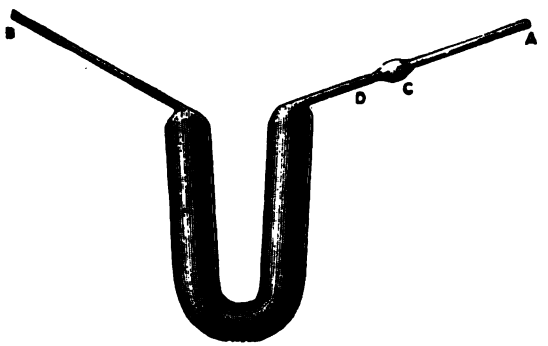


FIG. 7.

capillaries. The oil should be sucked into the tube through the opening, B, by means of a small india-rubber tube fixed on to the end, A, up to the small glass bulb, C. The tube is then placed in a beaker of water at the desired temperature, the bent arms serving to support it on the side of the beaker. Owing to its small content, from 2 to 5 c.c., it very rapidly acquires the temperature of the water, and by gently tilting the end, A, upwards, the oil runs out at B until it just reaches the graduation mark, D. Taking care to wipe off the last drop of oil exuding at B, the tube is again levelled, when the liquid flows back into the bulb, so obviating any possibility

of loss. It is then carefully wiped and suspended by a copper wire loop to the hook on the balance and weighed, and the specific gravity calculated from the weight of the oil and the weight of the corresponding volume of water. The accuracy of these tubes depends on the fineness of the capillaries and the rapidity with which their contents assume the exact temperature of the water in which the tube is immersed.

OPTICAL METHODS.

1. Refraction.

The author and several other chemists have for some years past persistently advocated the use of the refractometer in the examination of essential oils. Although this determination was regarded as of little use by many chemists, it is now generally recognised that it is indispensable. But its value is only to be properly estimated by a very careful consideration of the results obtained.

The refractive index of a given sample of oil is in most cases of very little value in indicating adulteration. There are certain well-recognised exceptions, where the oil and the adulterant have refractive indices which vary very widely. Such, for example, is the case with otto of roses and geraniol, or aniseed oil and petroleum. But the chief value of this determination lies in a careful examination of the various fractions obtained when an oil is distilled *in vacuo*. Here a consideration of the boiling points, specific gravity, optical rotation and refractive index of the various fractions will lead to most important indications. For example, an oil of peppermint adulterated with, on the one hand, a small quantity of copaiba or cedar-wood oil, and, on the other hand, with a small quantity of glyceryl acetate, would give a refractive index not much different from that of the genuine oil. But when distilled *in vacuo* and the residues or high boiling fractions examined, the high index in the one case

would at once suggest the presence of sesquiterpene bodies, whilst in the other case the very low index would indicate bodies belonging to the open-chain series.

Experience alone will enable one to make the best use of these indications, but it is important that as many figures should be available as possible. The following table embraces the results obtained on a very large number of samples of authentic origin, and were all determined with either a Zeiss refractometer or a Pulfrich instrument. Of these the Pulfrich instrument is the more elaborate, but the Zeiss Abbé refractometer, which is illustrated below, is the most useful instrument for ordinary work. Its great advantage lies in the fact that it requires only a few drops of fluid for a determination, and gives results which are accurate to one or two points in the fourth place of decimals. The author has made a very large number of determinations with it, and finds it to be absolutely reliable. Refractive indices between 1·3 and 1·7 can be determined by it, which figures cover the range found in essential oils. The following is the method of using this instrument :—

The method of measurement is based upon the observation of the position of the border line of the total reflection in relation to the faces of a prism of flint-glass, into which the light from the substance under investigation enters by the action of refraction.

The refractometer is mainly composed of the following parts :—

1. The double Abbé prism, which contains the fluid and can be rotated on a horizontal axis by means of an alidade.

2. A telescope for observing the border line of the total reflection which is formed in the prism.

3. A sector rigidly connected with the telescope, on which divisions (representing refractive indices) are engraved.

The double prism consists of two similar prisms of flint-

glass, each cemented into a metal mount and having a refractive index $n^d = 1{\cdot}75$; the fluid to be investigated (a few drops) is deposited between the two adjoining inner faces of the prisms in the form of a thin stratum (about 0·15 mm.

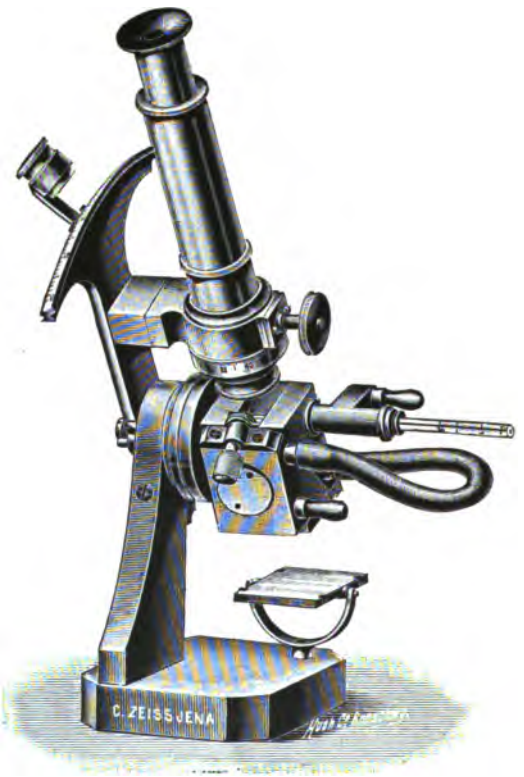


FIG. 8.

The daylight which falls upon the mirror passes through the double prism closed for the purpose of measurement, into the telescope; the arrows indicate the direction of the circulation of hot water round the prisms to retain a constant temperature. The magnifier is fitted with a reflector, not shown in the figure.

thick). The former of the two prisms, that farther from the telescope (which can be folded up or be removed), serves solely for the purpose of illumination, while the border line is formed in the second flint prism.

The border line is brought within the field of the telescope by rotating the double prism by means of the alidade in the following manner. Holding the sector, the alidade is moved from the initial position, at which the index points to n_d = 1·3, in the ascending scale of the refractive indices until the originally entirely illuminated field of view is encroached upon, from the direction of its lower half, by a dark portion; the line dividing the bright and the dark half of the field then is the "border line". When daylight or lamp light is being employed, the border line, owing to the total reflection and the refraction caused by the second prism, assumes at first the appearance of a band of colour, which is quite unsuitable for any exact process of adjustment. The conversion of this band of colour into a colourless line, sharply dividing the bright and dark portions of the field, is effected by a compensator.

The compensator, which finds its place in the prolongation of the telescope tube beyond the objective, *i.e.*, at a point between the objective and the double prism, consists of two similar Amici prisms, of direct vision for the D-line and rotated simultaneously, though in opposite directions, round the axis of the telescope by means of the screw head. In this process of rotation the dispersion of the compensator passes through every value from zero (when the refracting edges of the two Amici prisms are parallel and on different sides of the optical axis) up to double the amount of the dispersion of a single Amici prism (the refracting edges being parallel and on the same side of the axis). The above-mentioned dispersion of the border line, which appears in the telescope as a band of colour, can thus be rendered innocuous by rotating the screw head, thereby giving the compensator an equal, but opposite, dispersion. The opposite equal dispersions will then neutralise each other, with the result that the border line appears colourless and sharply defined.

The border line is now adjusted upon the point of intersection of the crossed lines by slightly inclining the double prism to the telescope by means of the alidade. The position of the pointer on the graduation of the sector is then read off by the aid of the magnifier attached to the alidade. The reading supplies the refractive index n_d of the substance under investigation itself, without any calculation.

As the refractive index of fluids varies with their temperature, it is of importance to know the temperature of the fluid contained in the double prism during the process of measurement.

If, therefore, it be desired to measure a fluid with the highest degree of accuracy attainable (to within 1 or 2 units of the fourth decimal of n_d) it is absolutely necessary to the fluid, or rather the double prism containing it, to a definite known temperature and to keep it constant.

TABLE OF REFRACTIVE INDICES. (FOR THE D-LINE AT 20° C.)

Almonds (bitter)	1·5500 to 1·5570	Lemongrass (East Indian)	1·4800 to 1·4850
Anethol	1·5600	Lemongrass (West Indian)	1·4800 to 1·4900
Aniseed	1·5530 to 1·5580	Lemon oil	1·4735 to 1·4765
Bergamot	1·464 to 1·4690	Neroli oil	1·4720 to 1·4760
Cajuput	1·4620 to 1·4685	Orange oil	1·4710 to 1·4755
Camphor oil (light)	1·4600 to 1·4710	Petit-grain oil	1·4620 to 1·4640
Copaiba	1·500 to 1·5100	Peppermint oil	1·4620 to 1·4730
Dill	1·4800 to 1·4900	Pimento oil	1·5100 to 1·5330
Cardamoms	1·4600 to 1·4680	Pennyroyal oil	1·4800 to 1·4825
Caraway	1·4870 to 1·4975	Rose oil (otto) at 25°	1·4580 to 1·4645
Cloves	1·5300 to 1·5360	Rosemary oil	1·4660 to 1·4710
Cassia	1·5920 to 1·5990	Rue oil	1·4350 to 1·4400
Cinnamon	1·5650 to 1·5770	Santal oil	1·5000 to 1·5080
Citronella (Ceylon)	1·4800 to 1·4850	Santal oil (so called, West Indian)	1·5080 to 1·5120
,, (Java)	1·4650 to 1·4675	Sassafras oil	1·5250 to 1·5350
Cubebs	1·4880 to 1·4960	Spike lavender oil	1·4650 to 1·4680
Eucalyptus globulus	1·4620 to 1·4650	Thyme oil	1·4850 to 1·4950
Geranium (French)	1·4600 to 1·4680	Turpentine oil	1·4700 to 1·4750
,, (so called, Indian)	1·4850 to 1·4920	Ylang-Ylang oil	1·4930 to 1·4965
Juniper	1·4710 to 1·4785	Wintergreen oil	1·5310 to 1·5380
Lavender	1·4625 to 1·4675		

The above determinations have in nearly every case been made by the author, in some cases by C. T. Bennett, and

cover a very large number of samples. Figures for the less common oils are not given as there is at present an insufficiency of reliable data. It is to be remembered that oils, after keeping for a certain time, commence to oxidise, and their refractive index increases. The refractive index of most of the well-defined constituents of the more commonly occurring oils should be looked for under the respective compounds.

2. Polarimetry.

The polarimeter is an instrument with which the essential oil chemist cannot possibly dispense. The hypothesis, first seriously enunciated by Le Bel and van t'Hoff, that substances which contained an asymmetric carbon atom (*i.e.*, a carbon atom directly united to four different atoms or radicles) were capable of rotating the plane of polarisation of a beam of polarised light, has now become a fundamental theory of organic chemistry. The majority of essential oils contain one or more components containing such a carbon atom, and so possess the power of effecting this rotation. In general, the extent to which a given oil can produce this effect is fairly constant, so that it can be used, within limits, as a criterion of the purity or otherwise of the oil.

Without discussing the theories of the polarisation of light it will be desirable to briefly illustrate the fundamental principles upon which their application depends. Ordinary light consists of transverse vibrations in numerous planes in which is no polarity or *two-sidedness*, if the expression is justifiable; whilst plane polarised light consists of vibrations in one plane only. This may be roughly illustrated in the following manner. If a string, fixed at its ends, be plucked it will vibrate in a certain plane dependent on the direction of the plucking. If the string be passed through a slit, just wider than it is itself, in a piece of cardboard, so that the slit is in the direction of the vibrations, these will not be

interfered with; but if the slit be turned round, the vibrations will be interfered with, and when it is at right angles to the direction of the vibrations, they will be totally suppressed. Light waves (for convenience, the expression, a ray of light, is more general) may be plane polarised in several ways, so that the vibrations in the one plane may be similarly interfered with, and upon this depends the use of the polarimeter. This instrument, of which the theory is described a little more fully in the footnote,[1] is constructed on several different

[1] The theory of the half-shadow polarimeter is, briefly, as follows. The light, of approximately constant refrangibility, falls on the polarising Nicol's prism, which is a rhomb of calc-spar cut obliquely by a plane perpendicular to the principal section. The cut faces are polished and cemented together again by a thin film of Canada balsam. Calc-spar is a doubly refracting substance, and in the ordinary way the incident ray is divided by the spar into two rays, the ordinary and the extraordinary, the former following the ordinary laws of refraction, the latter behaving abnormally. Two rays, then, will be found to emerge. But the refractive index of the balsam is greater than that of the spar for the extraordinary ray, and less than that for the ordinary ray, both of which are plane polarised. According to the usual laws of refraction, total reflection can only occur in passing from a more to a less refracting medium. Hence the extraordinary ray will always be transmitted, but by arranging the angle of incidence properly the ordinary ray can be totally reflected. Hence only the extraordinary ray now falls on to the Laurent plate, and it is in a plane polarised condition. This plate is made of quartz or gypsum over one-half of the field, and plain glass over the other. It is a doubly refracting substance and refracts the incident ray as ordinary and extraordinary rays. The thickness is so adjusted that it introduces a retardation of $\frac{1}{2}\lambda$ (where λ is the wave length of the light used) between the two rays. Consequently, the light emerges plane polarised from the crystalline plate, but the planes of polarisation of the rays emerging from the two halves will be inclined at an angle 2α, if α is the inclination of the incident single polarised ray to the optical axis of the quartz. Hence when this plate, with its two polarised rays, is viewed through the analysing Nicol, the two halves will be in general unequally illuminated, except when the principal plane of the Nicol be parallel to the optical axis of the crystalline plate. In this position we have the zero point of the instrument. The insertion of an optically active liquid destroys this condition by rotating the plane of polarisation, and the angle through which it is necessary to rotate the analyser in order to restore the "equal shadows" measures the rotation of the plane of polarisation.

Another simple instrument known as the *Biquartz* polariser depends on a rather different principle. Here two semicircular plates of quartz are

principles, of which by far the most useful for all general purposes is the Laurent half-shadow instrument. In the annexed diagram, A is a small telescope, B is a magnifying glass used to read the graduation on the dial and vernier, C is one of the verniers, D is a dial graduated to half degrees, E is the analysing Nicol's prism (a specially prepared prism of calc-spar, capable of polarising light) which is fixed to the graduated dial and telescope, F is the groove in which tubes containing the liquids to be examined are inserted, H is a pointer attached to the polarising Nicol's prism, G is the fixed Laurent plate (*vide infra*), and J is a plate of bichromate of potassium.

This apparatus can only be used with sodium light, as for quantitative results light of definite refrangibility must be used. A Bunsen lamp of convenient construction, into the flame of which a little common salt can be introduced on a platinum wire, is placed about 4 or 5 inches from the end J. The light is further sifted by means of the bichromate

placed in juxtaposition, each cut at right angles to its axis, one possessing *dextro-* and the other *laevo*-rotatory power. The two plates are of the same thickness, and produce equal rotations in opposite directions. The incident light in this case is white, and the lights of different refrangibilities are rotated through different angles. Hence when viewed by an analysing Nicol, waves of different refrangibilities will be quenched in the two halves, and they will in general appear of different colours. When the principal plane of the analyser, however, is parallel to the direction of the incident vibrations, the two halves will always be of the same colour, dependent on the complementary colours which are quenched. By suitably adjusting the thickness of the plate, the brilliant yellow may be quenched, and the delicate gray-violet tint, known as the tint of passage (Biot's *teinte sensible*), appears when both halves have the same colour. This point, the zero point of the apparatus, is easily fixed, for the slightest rotation to the right or left renders one-half of the field blue and the other red. Having set the instrument, it is found that when an optically active substance is introduced, the tint of passage disappears, and the analyser must be rotated in order to restore it, according to the optical activity of the substance.

To most observers it is easier to obtain equal illumination in the two halves of the field than to correctly obtain the tint of passage, hence the popularity of the former apparatus.

plate, so that light approximately corresponding to the D line of the spectrum falls on to the polariser, and that which passes through is plane polarised. The plate G is a special contrivance, half of which is made of quartz or gypsum, and the other half of plain glass; the thickness of this is carefully graduated, and the result—the optical theory of which need not here be discussed—is that when the analyser is in a certain position with reference to the polariser and plate, the two halves of this plate appear equally illuminated. By adjusting

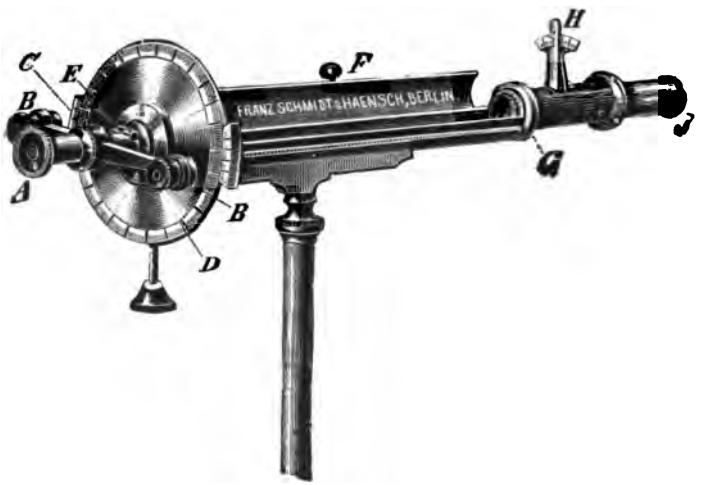


FIG. 9.

the prisms by means of the movable pointer, H, and the screw, E, which govern the delicacy of the instrument, the zero marks on the dial and on the vernier are made to correspond when the position of equal illumination is attained. A slight rotation of the analyser in either direction by means of the projecting screw handle at once causes the two halves of the field to become unequally illuminated. Having set the instrument at zero, a tube containing an optically active liquid is inserted in the groove, F. It will now be found that

the analyser has to be rotated a certain number of degrees either to the right or the left in order to restore the position of equal illumination of the two halves of the field. This is the angle through which the plane of polarisation has been rotated. The beginner will find a little difficulty in using this instrument; for example, when examining oils with high rotations or when the dial has been rotated too far, and has been taken beyond the range of sensitiveness; half an hour with some one who understands the instrument will explain its use far better than pages of printed matter. The rotation of the dial in the direction of the movement of the hands of the clock, as the observer sees it, is conventionally termed dextro-rotation, and conversely. In general, the *optical rotation* is expressed for a column of 100 mm. The specific rotary power is a different figure, and is expressed by the symbol $[a]$, and, taking the decimetre as the unit of length for this purpose, is the observed rotation in the decimetre tube divided by the specific gravity of the liquid. It is to be noted, however, that the expression $[a]$ is very frequently used to mean the observed rotation for 100 mm. The molecular rotation refers of course only to pure compounds and not to mixtures, and need not be discussed here, otherwise than to mention that it is the product of the specific rotary power and the molecular weight. In the sequel, the optical rotation will be understood to refer to the rotation produced by a column 100 mm. long, unless otherwise mentioned.

Melting and Solidifying Points.

Many oils possess the property of becoming solid at temperatures slightly below the ordinary, and a determination of the solidifying or melting points becomes an important criterion of purity in these cases. The melting point is not usually the same as the solidifying point, on account of the peculiar properties of bodies, included under the term

superfusion, etc. In addition, the temperature recorded differs somewhat with the method used in the determination. For general work the following apparatus gives the best results in a convenient manner.

Here the outer vessel contains a sufficient quantity of the freezing mixture, such as a mixture of ice and salt,

FIG. 10.

or a solution of one of the usual salts. The longer test tube acts as an air cover to the inner tube in which the thermometer is placed. A small quantity of the oil—just enough to cover the bulb of the thermometer—is placed in this tube, and in certain cases the platinum stirrer is used. The melting point is determined by freezing the oil and then removing the freezing mixture and allowing the temperature

to rise slowly, and noting the temperature at which liquefaction takes place. The solidification point is determined by cooling the oil down without disturbing it until the temperature is clearly below the point of solidification. A slight agitation of the stirrer will now usually induce solidification, if not, the introduction of a crystal of the compound solidifying—anethol, for example, in the case of aniseed oil —will do so. A disengagement of heat occurs on solidification, which causes the thermometer to rise. The maximum reading during the process of solidifying may be regarded as the solidifying point.

Boiling Point and Distillation.

The determination of the temperature at which an oil begins to boil is often of importance, as is also the percentage of the oil which distils within definite limits of temperature. The results obtained in distillation processes must however be interpreted very carefully, as the *quantitative* results depend so largely on the exact conditions of distillation. For ordinary purposes, an ordinary Wurtz flask is useful for determining the temperature at which the liquid first boils, but when an examination of any of the fractions or any estimation of the quantity boiling between given temperatures is needed, a fractional distillation flask is better. These flasks are illustrated on page 114.

It is often advisable to distil or fractionate an oil under reduced pressure, especially when the constituents decompose when boiled at atmospheric pressures.

The value of fractional distillation in the examination of essential oils cannot be overestimated. The various fractions may be examined and their specific gravities, optical rotations and refractive indices determined. The combination of these figures will often give the experienced analyst the most useful information and save him many hours' needless work.

Experience alone, however, will teach the chemist to make the fullest use of the results so obtained. In most cases distillation under reduced pressure is necessary on account of the risk of decomposing the various constituents of the oil. The use of a Brühl receiver (or any similar contrivance), which is easily obtained from any apparatus maker, saves the necessity of breaking the vacuum when collecting the different fractions.

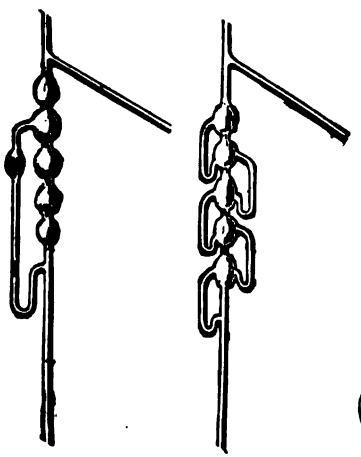


FIG. 11. Fractionating Columns.

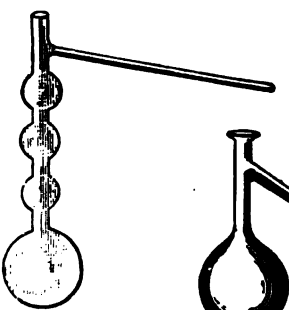


FIG. 12. Fractionating Flask.

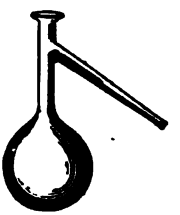


FIG. 13. Wurtz Flask.

QUANTITATIVE ESTIMATIONS OF CONSTITUENTS.

Very frequently it is necessary to make a quantitative determination of one or more of the bodies occurring in an essential oil. The methods used in these cases are of course exceedingly numerous, and in the present paragraph only a few of the most typical and generally employed will be referred to. It should be understood, however, that certain of these quantitative methods, as applied to complex organic mixtures, are not nearly so exact as quantitative methods of

inorganic analysis, but being worked in a uniform and definite method, the results are always strictly comparable.

The Determination of Esters.—Esters, or salts of alkyl radicles, such as linalyl acetate, etc., are frequently the most important constituents of essential oils. Their importance is especially noteworthy in such cases as lavender, bergamot, peppermint and wintergreen oils, and their estimation is very frequently necessary. The principle upon which this depends is the fact that most esters are decomposed by solution of caustic alkali (preferably in alcohol) according to the equation—

$$R\bar{A} + KOH = R.OH + K\bar{A},$$

where R is the alkyl, and $\bar{A}$ the acid, radicle.

To use this principle for the estimation, from 2 to 5 grammes of the oil, according to the magnitude of its ester content, are exactly weighed into a small flask capable of holding about 150 to 250 c.c., and from 15 to 25 c.c. of solution of caustic potash in alcohol are added. The strength of this should be approximately half-normal. The whole is then boiled in the water bath under a reflux condenser for an hour. It is then diluted with water and the excess of potash is estimated by titration with semi-normal sulphuric acid, using phenol-phthalein as an indicator. To determine the amount of potash originally employed, it is best to perform a blank experiment with the same quantity of potash solution, merely omitting the oil, so that the blank and the oil have been treated in an exactly similar way. The difference in the two titrations gives the amount of potash used in decomposing the esters. If any free acids are present these will have neutralised some of the potash, and it is then necessary to determine by a preliminary titration how much is used for this purpose, and to deduct the result from the total quantity of potash used.

The number of milligrammes of KOH used to saponify 1

gramme of the oil is termed the saponification or ester number. From this figure, which is now known, the percentage of esters present in a given oil may be rapidly calculated from the formula

$$\frac{M \times A}{560} = \text{percentage of ester,}$$

where M is the molecular weight of the ester, and A the ester number. (This is assuming, as is usually the case, that the ester is a combination of a monobasic acid with a monatomic alcohol.)

The Determination of Free Alcohols.—Many oils contain large quantities of free alcohols, such as geraniol or borneol. The only generally convenient way of estimating these depends on the conversion of the alcohols into their acetic esters, and then saponifying these in the manner just described. From 10 to 20 grammes of the oil (spike, sandalwood and geranium are typical) are boiled under a reflux condenser for one and a half hours with an equal volume of acetic anhydride and 10 per cent. of its weight of anhydrous sodium acetate. After the liquid has cooled, it is diluted with water and allowed to stand in the water bath for fifteen minutes in order to decompose the excess of acetic anhydride. The liquid is then transferred to a separator and repeatedly washed with distilled water until the wash water is perfectly neutral in reaction. The oil is then separated and the last traces of water removed by digestion with ignited acid potassium sulphate. About 2 to 5 grammes, depending on the alcohol content of the acetylated (esterified) oil, are then saponified as described above. The amount of *ester* in the *acetylated* oil is easily calculated, but to convert this into the percentage of *free alcohol* in the original oil requires a more tedious calculation. The following formula can be used for this:—

$$x = \frac{N \times M}{10(W - \cdot 042N)},$$

where x is the percentage of the alcohol in the *original* oil, M is the molecular weight, and N is the number of c.c. of normal alkali used, and W the weight of the *acetylated* oil. Here the factor ·042N is on account of the increase of the weight due to acetylation. This formula is only true if the original oil contains no esters. In cases where esters and alcohols occur together the best method is to—

(1) Estimate the esters in the original oil by a preliminary saponification of a small quantity.

(2) Saponify about 20 grammes and separate the resulting oil, which now contains all the alcohols in the free state.

(3) Estimate the total alcohols in 2 by the acetylation process.

(4) Calculate the total alcohols in the original oils from 3, by allowing for the decrease in weight of 1 when saponified.

(5) Deduct the alcohols combined as esters from the total alcohols, which gives the amount of free alcohols.

In these estimations it is necessary to calculate all the esters and all the alcohols to one formula, expressing the result, for instance, as menthyl acetate, although as a matter of fact small quantities of the corresponding propionate and butyrate may also be present, which it is impossible to estimate separately.

In certain cases the results thus obtained are very nearly scientifically accurate, but in certain cases the alcohol breaks down under the influence of the acetic anhydride and the results are considerably lower than the truth, the variation depending entirely on the conditions of the experiment, which should therefore be kept constant as above recommended. Linalol and terpineol are two cases in point. To meet such cases Boulez has recommended diluting 5 grammes of the oil with 25 grammes of turpentine, and then boiling with 40 c.c. of acetic anhydride and 3 to 4 grammes of pure sodium acetate. A blank experiment to allow for the "alcohol value" of the

turpentine must be performed, and the proper deduction made. It is claimed by Boulez that this method yields accurate results, but, although in the case of terpineol the results are fairly good, the process does not give scientifically accurate results.

The following tables have been prepared by Messrs. Schimmel & Co., who have allowed them to be reproduced here, in order to save calculations. Having determined the saponification value of the oil before or after acetylation, the amounts of esters or alcohols respectively can be calculated. It must be borne in mind that the alcohol values are only strictly accurate when there are no esters present in the oil. Table I. gives the values for alcohols of the formula $C_{10}H_{18}O$ and $C_{10}H_{20}O$ (geraniol and citronellol) and their acetic esters. Table II. gives the corresponding values for the alcohols $C_{15}H_{24}O$ and $C_{15}H_{26}O$. Table III. gives the ester values for geranyl tiglinate.

TABLE I.

$C_{10}H_{18}O$				$C_{10}H_{20}O$			
Sap. fig.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	Sap. fig.
1	0·35	0·28	0·27	0·35	0·28	0·28	1
2	0·70	0·55	0·55	0·71	0·56	0·56	2
3	1·05	0·83	0·83	1·06	0·84	0·84	3
4	1·40	1·10	1·10	1·41	1·11	1·12	4
5	1·75	1·38	1·38	1·77	1·39	1·40	5
6	2·10	1·65	1·66	2·12	1·67	1·68	6
7	2·45	1·93	1·94	2·47	1·95	1·96	7
8	2·80	2·20	2·21	2·83	2·23	2·24	8
9	3·15	2·48	2·49	3·18	2·51	2·52	9
10	3·50	2·75	2·77	3·54	2·79	2·81	10
11	3·85	3·03	3·05	3·89	3·06	3·09	11
12	4·20	3·30	3·33	4·24	3·34	3·37	12
13	4·55	3·58	3·61	4·60	3·62	3·66	13
14	4·90	3·85	3·89	4·95	3·90	3·94	14
15	5·25	4·13	4·17	5·30	4·18	4·23	15
16	5·60	4·40	4·45	5·66	4·46	4·51	16
17	5·95	4·68	4·74	6·01	4·74	4·80	17
18	6·30	4·95	5·02	6·36	5·01	5·08	18
19	6·65	5·23	5·30	6·72	5·29	5·37	19
20	7·00	5·50	5·58	7·07	5·57	5·66	20
21	7·35	5·78	5·87	7·42	5·85	5·94	21
22	7·70	6·05	6·15	7·78	6·13	6·23	22
23	8·05	6·33	6·44	8·13	6·41	6·52	23
24	8·40	6·60	6·72	8·49	6·69	6·81	24
25	8·75	6·88	7·01	8·84	6·96	7·10	25
26	9·10	7·15	7·29	9·19	7·24	7·39	26
27	9·45	7·43	7·58	9·55	7·52	7·68	27
28	9·80	7·70	7·87	9·90	7·80	7·97	28
29	10·15	7·98	8·15	10·25	8·08	8·26	29
30	10·50	8·25	8·44	10·61	8·36	8·55	30
31	10·85	8·53	8·73	10·96	8·64	8·84	31
32	11·20	8·80	9·02	11·31	8·91	9·13	32
33	11·55	9·08	9·31	11·67	9·19	9·43	33
34	11·90	9·35	9·59	12·02	9·47	9·72	34
35	12·25	9·63	9·88	12·37	9·75	10·01	35
36	12·60	9·90	10·17	12·73	10·03	10·31	36
37	12·95	10·18	10·47	13·08	10·31	10·60	37
38	13·30	10·45	10·76	13·44	10·59	10·90	38
39	13·65	10·73	11·05	13·79	10·86	11·19	39
40	14·00	11·00	11·34	14·14	11·14	11·49	40
41	14·35	11·28	11·63	14·50	11·42	11·78	41
42	14·70	11·55	11·93	14·85	11·70	12·08	42
43	15·05	11·83	12·22	15·20	11·98	12·38	43
44	15·40	12·10	12·51	15·56	12·26	12·68	44
45	15·75	12·38	12·81	15·91	12·54	12·97	45
46	16·10	12·65	13·10	16·26	12·81	13·27	46
47	16·45	12·93	13·40	16·62	13·09	13·57	47
48	16·80	13·20	13·69	16·97	13·37	13·87	48
49	17·15	13·48	13·99	17·32	13·65	14·17	49
50	17·50	13·75	14·29	17·68	13·93	14·47	50

TABLE I. (*continued*).

$C_{10}H_{18}O$				$C_{10}H_{20}O$			
Sap. fig.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	Sap. fig.
51	17·85	14·03	14·58	18·03	14·21	14·77	51
52	18·20	14·30	14·88	18·39	14·49	15·07	52
53	18·55	14·58	15·18	18·74	14·76	15·38	53
54	18·90	14·85	15·48	19·09	15·04	15·68	54
55	19·25	15·13	15·77	19·45	15·32	15·98	55
56	19·60	15·40	16·07	19·80	15·60	16·28	56
57	19·95	15·68	16·38	20·15	15·88	16·59	57
58	20·30	15·95	16·68	20·51	16·16	16·89	58
59	20·65	16·23	16·98	20·86	16·44	17·20	59
60	21·00	16·50	17·28	21·21	16·71	17·50	60
61	21·35	16·78	17·58	21·57	16·99	17·81	61
62	21·70	17·05	17·88	21·92	17·27	18·11	62
63	22·05	17·33	18·18	22·27	17·55	18·42	63
64	22·40	17·60	18·49	22·63	17·83	18·73	64
65	22·75	17·88	18·79	22·98	18·11	19·04	65
66	23·10	18·15	19·10	23·34	18·39	19·34	66
67	23·45	18·43	19·40	23·69	18·66	19·65	67
68	23·80	18·70	19·70	24·04	18·94	19·96	68
69	24·15	18·98	20·01	24·40	19·22	20·27	69
70	24·50	19·25	20·32	24·75	19·50	20·58	70
71	24·85	19·53	20·62	25·10	19·78	20·89	71
72	25·20	19·80	20·93	25·46	20·06	21·20	72
73	25·55	20·08	21·24	25·81	20·34	21·51	73
74	25·90	20·35	21·55	26·16	20·61	21·83	74
75	26·25	20·63	21·85	26·52	20·89	22·14	75
76	26·60	20·90	22·16	26·87	21·17	22·45	76
77	26·95	21·18	22·47	27·22	21·45	22·77	77
78	27·30	21·45	22·78	27·58	21·73	23·08	78
79	27·65	21·73	23·09	27·93	22·01	23·39	79
80	28·00	22·00	23·40	28·29	22·29	23·71	80
81	28·35	22·28	23·72	28·64	22·56	24·02	81
82	28·70	22·55	24·03	28·99	22·84	24·34	82
83	29·05	22·83	24·34	29·35	23·12	24·66	83
84	29·40	23·10	24·65	29·70	23·40	24·97	84
85	29·75	23·38	24·97	30·05	23·68	25·29	85
86	30·10	23·65	25·28	30·41	23·96	25·61	86
87	30·45	23·93	25·60	30·76	24·24	25·93	87
88	30·80	24·20	25·91	31·11	24·51	26·25	88
89	31·15	24·48	26·23	31·47	24·79	26·57	89
90	31·50	24·75	26·54	31·82	25·07	26·89	90
91	31·85	25·03	26·86	32·17	25·35	27·21	91
92	32·20	25·30	27·18	32·53	25·63	27·53	92
93	32·55	25·58	27·49	32·88	25·91	27·85	93
94	32·90	25·85	27·81	33·24	26·19	28·17	94
95	33·25	26·13	28·13	33·59	26·46	28·49	95
96	33·60	26·40	28·45	33·94	26·74	28·82	96
97	33·95	26·68	28·77	34·30	27·02	29·14	97
98	34·30	26·95	29·09	34·65	27·30	29·47	98
99	34·65	27·23	29·41	35·00	27·58	29·79	99
100	35·00	27·50	29·73	35·36	27·86	30·11	100

TABLE I. (*continued*).

$C_{10}H_{18}O$				$C_{10}H_{20}O$			
Sap. fig.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	Sap. fig.
101	35·35	27·78	30·05	35·71	28·14	30·44	101
102	35·70	28·05	30·37	36·06	28·41	30·77	102
103	36·05	28·33	30·70	36·42	28·69	31·09	103
104	36·40	28·60	31·02	36·77	28·97	31·42	104
105	36·75	28·88	31·34	37·12	29·25	31·75	105
106	37·10	29·15	31·67	37·48	29·53	32·08	106
107	37·45	29·43	31·99	37·83	29·81	32·41	107
108	37·80	29·70	32·32	38·19	30·09	32·74	108
109	38·15	29·98	32·64	38·54	30·36	33·07	109
110	38·50	30·25	32·97	38·89	30·64	33·40	110
111	38·85	30·53	33·30	39·25	30·92	33·73	111
112	39·20	30·80	33·62	39·60	31·20	34·06	112
113	39·55	31·08	33·95	39·95	31·48	34·39	113
114	39·90	31·35	34·28	40·31	31·76	34·73	114
115	40·25	31·63	34·61	40·66	32·04	35·06	115
116	40·60	31·90	34·94	41·01	32·31	35·39	116
117	40·95	32·18	35·27	41·37	32·59	35·73	117
118	41·30	32·45	35·60	41·72	32·87	36·06	118
119	41·65	32·73	35·93	42·07	33·15	36·40	119
120	42·00	33·00	36·26	42·43	33·43	36·73	120
121	42·35	33·28	36·60	42·78	33·71	37·07	121
122	42·70	33·55	36·93	43·14	33·99	37·41	122
123	43·05	33·83	37·26	43·49	34·26	37·75	123
124	43·40	34·10	37·60	43·84	34·54	38·08	124
125	43·75	34·38	37·93	44·20	34·82	38·42	125
126	44·10	34·65	38·27	44·55	35·10	38·76	126
127	44·45	34·93	38·60	44·90	35·38	39·10	127
128	44·80	35·20	38·94	45·26	35·66	39·44	128
129	45·15	35·48	39·27	45·61	35·94	39·78	129
130	45·50	35·75	39·61	45·96	36·21	40·13	130
131	45·85	36·03	39·95	46·32	36·49	40·47	131
132	46·20	36·30	40·29	46·67	36·77	40·81	132
133	46·55	36·58	40·63	47·02	37·05	41·16	133
134	46·90	36·85	40·97	47·38	37·33	41·50	134
135	47·25	37·13	41·31	47·73	37·61	41·84	135
136	47·60	37·40	41·65	48·09	37·89	42·19	136
137	47·95	37·68	41·99	48·44	38·16	42·53	137
138	48·30	37·95	42·33	48·79	38·44	42·88	138
139	48·65	38·23	42·67	49·15	38·72	43·23	139
140	49·00	38·50	43·02	49·50	39·00	43·58	140
141	49·35	38·78	43·36	49·85	39·28	43·92	141
142	49·70	39·05	43·71	50·21	39·56	44·27	142
143	50·05	39·33	44·05	50·56	39·84	44·62	143
144	50·40	39·60	44·39	50·91	40·11	44·97	144
145	50·75	39·88	44·74	51·27	40·39	45·32	145
146	51·10	40·15	45·09	51·62	40·67	45·67	146
147	51·45	40·43	45·44	51·97	40·95	46·02	147
148	51·80	40·70	45·78	52·33	41·23	46·38	148
149	52·15	40·98	46·13	52·68	41·51	46·73	149
150	52·50	41·25	46·48	53·04	41·79	47·08	150

TABLE I. (*continued*).

	$C_{10}H_{18}O$			$C_{10}H_{20}O$		
Sap. fig.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil
151	52·85	41·53	46·83	53·39	42·06	47·44
152	53·20	41·80	47·18	53·74	42·34	47·79
153	53·55	42·08	47·53	54·10	42·62	48·15
154	53·90	42·35	47·88	54·45	42·90	48·50
155	54·25	42·63	48·23	54 80	43·18	48·86
156	54·60	42·90	48·58	55·16	43·46	49·21
157	54·95	43·18	48·94	55·51	43·74	49·57
158	55·30	43·45	49·29	55·86	44·01	49·93
159	55·65	43·73	49·65	56·22	44·29	50·29
160	56·00	44·00	50·00	56·57	44·57	50·65
161	56·35	44·28	50·36	56·92	44·85	51·01
162	56·70	44·55	50·71	57·28	45·13	51·37
163	57·05	44·83	51·07	57·63	45·41	51·73
164	57·40	45·10	51·42	57·99	45·69	52·09
165	57·75	45·38	51·78	58·34	45·96	52·46
166	58·10	45·65	52·14	58·69	46·24	52·82
167	58·45	45·93	52·50	59·05	46·52	53·18
168	58·80	46·20	52·86	59·40	46·80	53·55
169	59·15	46·48	53·22	59·75	47·08	53·91
170	59·50	46·75	53·58	60·11	47·36	54·28
171	59·85	47·03	53·94	60·46	47·64	54·64
172	60·20	47·30	54·31	60·81	47·91	55·01
173	60·55	47·58	54·67	61·17	48·19	55·38
174	60·90	47·85	55·03	61·52	48·47	55·75
175	61·25	48·13	55·40	61·87	48·75	56·12
176	61·60	48·40	55·76	62·23	49·03	56·48
177	61·95	48·68	56·13	62·58	49·31	56·85
178	62·30	48·95	56·49	62·94	49·59	57·23
179	62·65	49·23	56·86	63·29	49·86	57·60
180	63·00	49·50	57·22	63·64	50·14	57·97
181	63·35	49·78	57·59	64·00	50·42	58·34
182	63·70	50·05	57·96	64·35	50·70	58·71
183	64·05	50·33	58·33	64·70	50·98	59·09
184	64·40	50·60	58·70	65·06	51·26	59·46
185	64·75	50·88	59·07	65·41	51·54	59·84
186	65·10	51·15	59·44	65·76	51·81	60·21
187	65·45	51·43	59·81	66·12	52·09	60·59
188	65·80	51·70	60·19	66·47	52·37	60·97
189	66·15	51·98	60·56	66·82	52·65	61·35
190	66·50	52·25	60·93	67·18	52·93	61·72
191	66·85	52·53	61·31	67·53	53·21	62·10
192	67·20	52·80	61·68	67·89	53·49	62·48
193	67·55	53·08	62·06	68·24	53·76	62·86
194	67·90	53·35	62·43	68·59	54·04	63·24
195	68·25	53·63	62·81	68·95	54·32	63·63
196	68·60	53·90	63·19	69·30	54·60	64·01
197	68·95	54·18	63·57	69·65	54·88	64·39
198	69·30	54·45	63·95	70 01	55·16	64·78
199	69·65	54·73	64·33	70·36	55·44	65·16
200	70·00	55·00	64·71	70·71	55·71	65·55

TABLE I. (*continued*).

$C_{10}H_{18}O$				$C_{10}H_{20}O$			
Sap. fig.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	Sap. fig.
201	70·35	55·28	65·09	71·07	55·99	65·98	201
202	70·70	55·55	65·47	71·42	56·27	66·32	202
203	71·05	55·83	65·85	71·77	56·55	66·71	203
204	71·40	56·10	66·23	72·13	56·83	67·09	204
205	71·75	56·38	66·62	72·48	57·11	67·48	205
206	72·10	56·65	67·00	72·84	57·39	67·87	206
207	72·45	56·93	67·39	73·19	57·66	68·26	207
208	72·80	57·20	67·77	73·54	57·94	68·65	208
209	73·15	57·48	68·16	73·90	58·22	69·04	209
210	73·50	57·75	68·55	74·25	58·50	69 44	210
211	73·85	58·03	68·93	74·60	58·78	69·83	211
212	74·20	58·30	69·32	74·96	59·06	70·22	212
213	74·55	58·58	69·71	75·31	59·34	70·62	213
214	74·90	58·85	70·10	75·66	59·61	71·01	214
215	75·25	59·13	70·49	76·02	59·89	71·41	215
216	75·60	59·40	70·88	76·37	60·17	71·80	216
217	75·95	59·68	71·28	76·72	60·45	72·20	217
218	76·30	59·95	71·67	77·08	60·73	72·60	218
219	76·65	60·23	72·06	77·43	61·01	73·00	219
220	77·00	60·50	72·45	77·79	61·29	73·40	220
221	77·35	60·78	72·85	78·14	61·56	73·80	221
222	77·70	61·05	73·25	78·49	61·84	74·20	222
223	78·05	61·33	73·64	78·85	62·12	74·60	223
224	78·40	61·60	74·04	79·20	62·40	75·00	224
225	78·75	61·88	74·44	79·55	62·68	75·40	225
226	79·10	62·15	74·84	79·91	62·96	75·81	226
227	79·45	62·43	75·23	80·26	63·24	76·21	227
228	79·80	62·70	75·63	80·61	63·51	76·62	228
229	80·15	62·98	76·03	80·97	63·79	77·02	229
230	80·50	63·25	76·44	81·32	64·07	77·43	230
231	80·85	63·53	76·84	81·67	64·35	77·83	231
232	81·20	63·80	77·24	82·03	64·63	78·24	232
233	81·55	64·08	77·64	82·38	64·91	78·65	233
234	81·90	64·35	78·05	82·74	65·19	79·06	234
235	82·25	64·63	78·45	83·09	65·46	79·47	235
236	82·60	64·90	78·86	83·44	65·74	79·88	236
237	82·95	65·18	79·27	83·80	66·02	80·29	237
238	83·30	65·45	79·67	84·15	66·30	80·71	238
239	83·65	65·73	80·08	84·50	66·58	81·12	239
240	84·00	66·00	80·49	84·86	66·86	81·53	240
241	84·35	66·28	80·90	85·21	67·14	81·95	241
242	84·70	66·55	81·31	85·56	67·41	82·36	242
243	85·05	66·83	81·72	85·92	67·69	82·78	243
244	85·40	67·10	82·13	86·27	67·97	83·20	244
245	85·75	67·38	82·54	86·62	68·25	83·61	245
246	86·10	67·65	82·96	86·98	68·53	84·03	246
247	86·45	67·93	83·37	87·33	68·81	84·45	247
248	86·80	68·20	83·78	87·69	69·09	84·87	248
249	87·15	68·48	84·20	88·04	69·36	85·29	249
250	87·50	68·75	84·62	88·39	69·64	85·71	250

TABLE I. (*continued*).

$C_{10}H_{18}O$				$C_{10}H_{20}O$			
Sap. fig.	Acetate	Alcohol	Alcohol in the orig. oil	Acetate	Alcohol	Alcohol in the orig. oil	Sap. fig.
251	87·85	69·03	85·03	88·75	69·92	86·14	251
252	88·20	69·30	85·45	89·10	70·20	86·56	252
253	88·55	69·58	85·87	89·45	70·48	86·98	253
254	88·90	69·85	86·29	89·81	70·76	87·41	254
255	89·25	70·13	86·71	90·16	71·04	87·83	255
256	89·60	70·40	87·13	90·51	71·31	88·26	256
257	89·95	70·68	87·55	90·87	71·59	88·69	257
258	90·30	70·95	87·97	91·22	71·87	89·11	258
259	90·65	71·23	88·40	91·57	72·15	89·54	259
260	91·00	71·50	88·82	91·93	72·43	89·97	260
261	91·35	71·78	89·25	92·28	72·71	90·40	261
262	91·70	72·05	89·67	92·64	72·99	90·83	262
263	92·05	72·33	90·10	92·99	73·26	91·27	263
264	92·40	72·60	90·52	93·34	73·54	91·70	264
265	92·75	72·88	90·95	93·70	73·82	92·13	265
266	93·10	73·15	91·38	94·05	74·10	92·57	266
267	93·45	73·43	91·81	94·40	74·38	93·00	267
268	93·80	73·70	92·24	94·76	74·66	93·44	268
269	94·15	73·98	92·67	95·11	74·94	93·87	269
270	94·50	74·25	93·10	95·46	75·21	94·31	270
271	94·85	74·53	93·54	95·82	75·49	94·75	271
272	95·20	74·80	93·97	96·17	75·77	95·19	272
273	95·55	75·08	94·40	96·52	76·05	95·63	273
274	95·90	75·35	94·84	96·88	76·33	96·07	274
275	96·25	75·63	95·28	97·23	76·61	96·51	275
276	96·60	75·90	95·71	97·59	76·89	96·96	276
277	96·95	76·18	96·15	97·94	77·16	97·40	277
278	97·30	76·45	96·59	98·29	77·44	97·84	278
279	97·65	76·73	97·03	98·65	77·72	98·29	279
280	98·00	77·00	97·47	99·00	78·00	98·73	280
281	98·35	77·28	97·91	99·35	78·28	99·18	281
282	98·70	77·55	98·35	99·71	78·56	99·63	282
283	99·05	77·83	98·80	100·06	78·84	100·08	283
284	99·40	78·10	99·24				
285	99·75	78·38	99·68				
286	100·10	78·65	100·13				

TABLE II.

$C_{15}H_{24}O$				$C_{15}H_{26}O$			
Ester number	% Acetate	% Alcohol	% Alcohol in the orig. oil	% Acetate	% Alcohol	% Alcohol in the orig. oil	Ester number
1	0·47	0·39	0·39	0·47	0·40	0·40	1
2	0·94	0·79	0·79	0·94	0·79	0·79	2
3	1·40	1·18	1·18	1·41	1·19	1·19	3
4	1·87	1·57	1·58	1·89	1·59	1·59	4
5	2·34	1·96	1·97	2·36	1·98	1·99	5
6	2·81	2·36	2·37	2·83	2·38	2·39	6
7	3·28	2·75	2·76	3·30	2·78	2·79	7
8	3·74	3·14	3·16	3·77	3·17	3·19	8
9	4·21	3·53	3·56	4·24	3·57	3·59	9
10	4·68	3·93	3·96	4·71	3·96	3·99	10
11	5·15	4·32	4·36	5·19	4·36	4·40	11
12	5·61	4·71	4·76	5·66	4·76	4·80	12
13	6·08	5·11	5·16	6·13	5·15	5·20	13
14	6·55	5·50	5·56	6·60	5·55	5·61	14
15	7·02	5·89	5·96	7·07	5·95	6·01	15
16	7·49	6·29	6·36	7·54	6·34	6·42	16
17	7·95	6·68	6·77	8·01	6·74	6·83	17
18	8·42	7·07	7·17	8·49	7·14	7·23	18
19	8·89	7·46	7·57	8·96	7·53	7·64	19
20	9·36	7·86	7·98	9·43	7·93	8·05	20
21	9·83	8·25	8·38	9·90	8·33	8·46	21
22	10·29	8·64	8·79	10·37	8·72	8·87	22
23	10·76	9·03	9·19	10·84	9·12	9·28	23
24	11·23	9·42	9·60	11·31	9·51	9·69	24
25	11·70	9·82	10·01	11·79	9·91	10·10	25
26	12·16	10·21	10·42	12·26	10·30	10·51	26
27	12·63	10·60	10·83	12·73	10·70	10·92	27
28	13·10	11·00	11·24	13·20	11·10	11·34	28
29	13·57	11·39	11·65	13·67	11·49	11·75	29
30	14·04	11·79	12·06	14·14	11·89	12·17	30
31	14·51	12·18	12·47	14·61	12·28	12·58	31
32	14·98	12·57	12·88	15·08	12·68	13·00	32
33	15·45	12·96	13·29	15·55	13·08	13·41	33
34	15·91	13·35	13·71	16·02	13·48	13·83	34
35	16·38	13·75	14·12	16·50	13·88	14·25	35
36	16·35	14·14	14·54	16·97	14·27	14·67	36
37	17·32	14·54	14·95	17·44	14·76	15·09	37
38	17·79	14·93	15·37	17·91	15·06	15·51	38
39	18·25	15·32	15·78	18·38	15·46	15·93	39
40	18·71	15·71	16·20	18·86	15·86	16·35	40
41	19·18	16·10	16·62	19·33	16·25	16·77	41
42	19·65	16·50	17·04	19·80	16·65	17·19	42
43	20·12	16·89	17·46	20·27	17·05	17·61	43
44	20·59	17·28	17·88	20·74	17·44	18·04	44
45	21·05	17·68	18·30	21·21	17·84	18·46	45
46	21·52	18·07	18·72	21·69	18·24	18·89	46
47	21·99	18·46	19·14	22·16	18·63	19·32	47
48	22·46	18·85	19·56	22·63	19·03	19·74	48
49	22·93	19·25	19·98	23·10	19·82	20·17	49
50	23·39	19·64	20·41	23·57	19·43	20·59	50

TABLE II. (*continued*).

$C_{15}H_{24}O$				$C_{15}H_{26}O$			
Ester number	% Acetate	% Alcohol	% Alcohol in the orig. oil	% Acetate	% Alcohol	% Alcohol in the orig. oil	Ester number
51	23·86	20·03	20·83	24·04	20·22	21·02	51
52	24·33	20·42	21·26	24·51	20·62	21·45	52
53	24·80	20·82	21·68	24·99	21·01	21·88	53
54	25·26	21·21	22·11	25·46	21·41	22·31	54
55	25·73	21·60	22·54	25·93	21·81	22·74	55
56	26·20	22·00	22·96	26·40	22·20	23·17	56
57	26·67	22·39	23·39	26·87	22·60	23·61	57
58	27·14	22·78	23·82	27·34	23·00	24·04	58
59	27·61	23·17	24·25	27·81	23·39	24·47	59
60	28·07	23·57	24·68	28·29	23·79	24·91	60
61	28·54	23·96	25·11	28·76	24·19	25·34	61
62	29·01	24·35	25·54	29·23	24·58	25·77	62
63	29·48	24·75	25·97	29·70	24·98	26·21	63
64	29·95	25·14	26·41	30·17	25·38	26·65	64
65	30·41	25·53	26·84	30·64	25·77	27·09	65
66	30·88	25·93	27·27	31·11	26·17	27·53	66
67	31·35	26·32	27·71	31·59	26·57	27·97	67
68	31·81	26·71	28·14	32·06	26·96	28·41	68
69	32·28	27·10	28·58	32·53	27·35	28·85	69
70	32·75	27·50	29·02	33·00	27·75	29·29	70
71	33·22	27·89	29·46	33·47	28·15	29·73	71
72	33·69	28·28	29·90	33·94	28·54	30·17	72
73	34·15	28·67	30·34	34·41	28·94	30·61	73
74	34·62	29·07	30·78	34·89	29·34	31·06	74
75	35·09	29·46	31·22	35·36	29·73	31·50	75
76	35·56	29·85	31·66	35·83	30·13	31·95	76
77	36·03	30·25	32·10	36·30	30·53	32·40	77
78	36·49	30·64	32·54	36·77	30·92	32·84	78
79	36·96	31·03	32·98	37·24	31·31	33·29	79
80	37·43	31·43	33·43	37·71	31·71	33·74	80
81	37·90	31·82	33·87	38·19	32·11	34·19	81
82	38·37	32·21	34·32	38·66	32·50	34·64	82
83	38·84	32·60	34·77	39·13	32·90	35·09	83
84	39·30	33·00	35·22	39·60	33·30	35·54	84
85	39·77	33·39	35·66	40·07	33·69	35·99	85
86	40·24	33·78	36·11	40·54	34·09	36·44	86
87	40·70	34·18	36·56	41·01	34·49	36·90	87
88	41·17	34·57	37·01	41·49	34·88	37·35	88
89	41·64	34·96	37·46	41·96	35·28	37·80	89
90	42·11	35·36	37·92	42·43	35·68	38·26	90
91	42·57	35·75	38·37	42·90	36·08	38·71	91
92	43·04	36·14	38·82	43·37	36·47	39·17	92
93	43·51	36·53	39·27	43·84	36·87	39·63	93
94	43·98	36·92	39·73	44·31	37·26	40·09	94
95	44·45	37·32	40·18	44·79	37·66	40·55	95
96	44·92	37·71	40·64	45·26	38·05	41·01	96
97	45·39	38·10	41·10	45·73	38·45	41·47	97
98	45·85	38·50	41·55	46·20	38·85	41·93	98
99	46·32	38·89	42·01	46·67	39·24	42·39	99
100	46·79	39·29	42·47	47·14	39·64	42·86	100

TABLE II. (*continued*).

$C_{15}H_{24}O$				$C_{15}H_{26}O$			
Ester number	Acetate %	Alcohol %	Alcohol in the orig. oil %	Acetate %	Alcohol %	Alcohol in the orig. oil %	Ester number
101	47·26	39·68	42·93	47·61	40·04	43·32	101
102	47·72	40·07	43·39	48·09	40·43	43·78	102
103	48·19	40·46	43·85	48·56	40·83	44·24	103
104	48·66	40·85	44·32	49·03	41·23	44·71	104
105	49·13	41·25	44·78	49·50	41·63	45·18	105
106	49·59	41·64	45·24	49·97	42·02	45·65	106
107	50·06	42·04	45·70	50·44	42·42	46·12	107
108	50·53	42·43	46·16	50·91	42·81	46·59	108
109	51·00	42·82	46·63	51·39	43·21	47·06	109
110	51·46	43·21	47·10	51·86	43·61	47·53	110
111	51·93	43·60	47·57	52·33	44·00	48·00	111
112	52·40	44·00	48·04	52·80	44·40	48·47	112
113	52·87	44·39	48·50	53·27	44·80	48·94	113
114	53·34	44·78	48·97	53·74	45·19	49·42	114
115	53·81	45·17	49·44	54·21	45·59	49·89	115
116	54·28	45·57	49·91	54·69	45·99	50·36	116
117	54·74	45·96	50·39	55·16	46·38	50·84	117
118	55·21	46·35	50·86	55·63	46·78	51·32	118
119	55·68	46·74	51·33	56·10	47·18	51·80	119
120	56·14	47·14	51·81	56·57	47·57	52·28	120
121	56·61	47·53	52·28	57·04	47·97	52·76	121
122	57·08	47·92	52·76	57·51	48·36	53·24	122
123	57·55	48·32	53·23	57·99	48·76	53·72	123
124	58·01	48·71	53·71	58·46	49·16	54·20	124
125	58·48	49·10	54·18	58·93	49·55	54·68	125
126	58·95	49·50	54·66	59·40	49·95	55·17	126
127	59·42	49·89	55·14	59·87	50·35	55·65	127
128	59·89	50·28	55·62	60·34	50·74	56·18	128
129	60·36	50·67	56·11	60·81	51·14	56·62	129
130	60·82	51·07	56·59	61·28	51·54	57·10	130
131	61·29	51·46	57·07	61·75	51·93	57·59	131
132	61·76	51·85	57·55	62·22	52·33	58·08	132
133	62·23	52·25	58·03	62·70	52·73	58·57	133
134	62·70	52·64	58·52	63·17	53·12	59·06	134
135	63·16	53·03	59·00	63·64	53·52	59·55	135
136	63·63	53·42	59·49	64·11	53·92	60·04	136
137	64·10	53·82	59·98	64·59	54·31	60·53	137
138	64·57	54·21	60·47	65·06	54·71	61·02	138
139	65·04	54·60	60·96	65·53	55·11	61·51	139
140	65·50	55·00	61·45	66·00	55·50	62·01	140
141	65·97	55·39	61·94	66·47	55·90	62·50	141
142	66·44	55·78	62·43	66·94	56·30	63·00	142
143	66·90	56·18	62·93	67·41	56·69	63·50	143
144	67·37	56·57	63·42	67·89	57·09	64·00	144
145	67·84	56·96	63·92	68·36	57·49	64·50	145
146	68·31	57·35	64·41	68·83	57·88	65·00	146
147	68·78	57·75	64·91	69·30	58·28	65·50	147
148	69·25	58·14	65·40	69·77	58·68	66·00	148
149	69·72	58·53	65·90	70·24	59·07	66·50	149
150	70·18	58·93	66·40	70·71	59·46	67·00	150

TABLE II. (*continued*).

$C_{15}H_{24}O$				$C_{15}H_{26}O$			
Ester number	% Acetate	% Alcohol	% Alcohol in the orig. oil	% Acetate	% Alcohol	% Alcohol in the orig. oil	Ester number
151	70·65	59·32	66·90	71·19	59·86	67·51	151
152	71·12	59·71	67·40	71·66	60·26	68·01	152
153	71·58	60·10	67·90	72·13	60·65	68·52	153
154	72·05	60·50	68·40	72·60	61·05	69·02	154
155	72·52	60·89	68·90	73·07	61·45	69·58	155
156	72·99	61·28	69·41	73·54	61·84	70·04	156
157	73·46	61·68	69·91	74·01	62·24	70·55	157
158	73·92	62·07	70·42	74·49	62·64	71·06	158
159	74·39	62·46	70·29	74·96	63·03	71·57	159
160	74·86	62·86	71·43	75·43	63·43	72·08	160
161	75·33	63·25	71·93	75·90	63·83	72·59	161
162	75·80	63·64	72·44	76·37	64·22	73·10	162
163	76·26	64·03	72·95	76·84	64·62	73·62	163
164	76·73	64·42	73·46	77·31	65·02	74·13	164
165	77·20	64·82	73·97	77·78	65·41	74·65	165
166	77·67	65·21	74·49	78·26	65·81	75·16	166
167	78·14	65·60	75·00	78·73	66·21	75·68	167
168	78·60	66·00	75·52	79·20	66·60	76·20	168
169	79·07	66·39	76·03	79·67	67·00	76·72	169
170	79·54	66·79	76·55	80·14	67·39	77·24	170
171	80·01	67·18	77·06	80·61	67·79	77·76	171
172	80·48	67·57	77·58	81·08	68·19	78·28	172
173	80·94	67·96	78·10	81·56	68·58	78·81	173
174	81·41	68·35	78·62	82·03	68·98	79·33	174
175	81·88	68·75	79·14	82·50	69·38	79·85	175
176	82·35	69·14	79·66	82·97	69·77	80·38	176
177	82·81	69·54	80·18	83·44	70·17	80·91	177
178	83·28	69·93	80·70	83·91	70·57	81·43	178
179	83·75	70·32	81·23	84·38	70·96	81·96	179
180	84·21	70·71	81·75	84·86	71·36	82·49	180
181	84·68	71·10	82·28	85·33	71·76	83·02	181
182	85·15	71·50	82·80	85·80	72·15	83·55	182
183	85·62	71·89	83·33	86·27	72·55	84·09	183
184	86·09	72·28	83·86	86·74	72·95	84·62	184
185	86·56	72·68	84·39	87·21	73·34	85·15	185
186	87·03	73·07	84·92	87·68	73·74	85·69	186
187	87·49	73·46	85·45	88·16	74·14	86·22	187
188	87·96	73·86	85·98	88·63	74·53	86·76	188
189	88·43	74·25	86·51	89·10	74·93	87·30	189
190	88·89	74·64	87·05	89·57	75·32	87·84	190
191	89·36	75·03	87·58	90·04	75·72	88·38	191
192	89·83	75·42	88·12	90·51	76·12	88·92	192
193	90·30	75·82	88·65	90·98	76·51	89·46	193
194	90·77	76·21	89·19	91·46	76·91	90·00	194
195	91·24	76·60	89·73	91·93	77·31	90·54	195
196	91·70	77·00	90·27	92·40	77·70	91·09	196
197	92·17	77·39	90·81	92·87	78·10	91·64	197
198	92·64	77·78	91·35	93·34	78·50	92·18	198
199	93·11	78·17	91·89	93·81	78·89	92·73	199
200	93·57	78·57	92·44	94·28	79·29	93·28	200

TABLE II. (*continued*).

$C_{15}H_{24}O$				$C_{15}H_{26}O$			
Ester number	% Acetate	% Alcohol	% Alcohol in the orig. oil	% Acetate	% Alcohol	% Alcohol in the orig. oil	Ester number
201	94·04	78·96	92·98	94·76	79·68	93·83	201
202	94·51	79·35	93·53	95·23	80·08	94·38	202
203	94·98	79·75	94·07	95·70	80·48	94·93	203
204	95·44	80·14	94·62	96·17	80·87	95·48	204
205	95·91	80·53	95·17	96·64	81·26	96·03	205
206	96·38	80·92	95·72	97·11	81·66	96·59	206
207	96·85	81·32	96·27	97·58	82·06	97·14	207
208	97·32	81·71	96·82	98·05	82·45	97·70	208
209	97·79	82·10	97·37	98·52	82·85	98·25	209
210	98·25	82·50	97·92	99·00	83·25	98·81	210
211	98·72	82·89	98·48	99·47	83·64	99·37	211
212	99·19	83·28	99·03	99·94	84·04	99·93	212
213	99·66	83·67	99·59	100·41	84·44	100·49	213
214	100·12	84·07	100·14				214

TABLE III.—GERANYL TIGLINATE: $C_4H_7CO_2C_{10}H_{17}$.

Ester number.	Per cent. Ester.	Ester number.	Per cent. Ester.	Ester number.	Per cent. Ester.	Ester number.	Per cent. Ester.	Ester number.	Per cent. Ester.
1	0·42	21	8·85	41	17·28	61	25·71	81	34·13
2	0·84	22	9·27	42	17·70	62	26·13	82	34·55
3	1·26	23	9·69	43	18·12	63	26·55	83	34·98
4	1·69	24	10·11	44	18·54	64	26·97	84	35·40
5	2·11	25	10·54	45	18·96	65	27·39	85	35·82
6	2·53	26	10·96	46	19·38	66	27·81	86	36·24
7	2·95	27	11·38	47	19·80	67	28·23	87	36·66
8	3·37	28	11·80	48	20·23	68	28·65	88	37·09
9	3·79	29	12·22	49	20·65	69	29·08	89	37·51
10	4·21	30	12·64	50	21·07	70	29·50	90	37·93
11	4·63	31	13·06	51	21·49	71	29·92	91	38·35
12	5·05	32	13·49	52	21·91	72	30·34	92	38·77
13	5·47	33	13·91	53	22·33	73	30·76	93	39·19
14	5·90	34	14·33	54	22·75	74	31·18	94	39·62
15	6·32	35	14·75	55	23·18	75	31·61	95	40·04
16	6·74	36	15·17	56	23·60	76	32·03	96	40·46
17	7·16	37	15·59	57	24·02	77	32·45	97	40·88
18	7·58	38	16·01	58	24·44	78	32·87	98	41·30
19	8·01	39	16·44	59	24·87	79	33·29	99	41·72
20	8·43	40	16·86	60	25·29	80	33·71	100	42·14

Absorption Processes.—Numerous constituents of essential oils, which are themselves insoluble in water, or practically so, readily form soluble compounds with certain inorganic bodies. Such, for example, are many aldehydes, which form soluble compounds with a solution of sodium bisulphite $NaHSO_3$, and phenols such as eugenol, which forms a soluble salt with potassium hydroxide. Upon this principle depend the quantitative absorption processes which are frequently used in the examination of essential oils.

The most useful method of determining the absorbable constituents is as follows. From 5 to 10 c.c. of the oil are measured carefully into a flask capable of holding about 200 c.c., having a long narrow neck graduated into $\frac{1}{10}$ c.c. Excess of the absorbing solution—in the case of cassia oil, for example, hot nearly saturated solution of sodium bisulphite, in the case of oil of cloves, aqueous solution of potash—is then added and the whole is well shaken and allowed to stand for a time. More of the solution is then added to nearly fill the flask and the whole is allowed to stand in the water bath until any crystals formed are dissolved, and the oily layer of unabsorbed residue rises to the surface. More solution is carefully poured in, and the oily layer forced up into the graduated neck, when its volume is read off. Two precautions must here be taken. Firstly, the temperature at which the oil is first measured, and that at which the unabsorbed residue is measured, must be identical. Secondly, it must be remembered that the measurements only give the volume percentages, hence to determine the percentage by weight it is necessary to know the specific gravity of the oil and of the non-absorbable residue. Of course, the latter can be separated and weighed, but the advantages of this are more than counterbalanced by the loss in weight experienced whilst removing the last traces of water.

Aldehydes and ketones are the bodies most usually esti-

mated by absorption, and although the use of sodium bisulphite is general, Burgess prefers the use of neutral sodium sulphite, and as he has carefully examined the various absorption processes, it is advisable to quote *in extenso* from his paper (*Analyst*, March, 1904). He classifies and criticises the various processes as follows:—

1. By treatment of the substance with a strong solution of bisulphite of soda or potash.

The directions for carrying out this process as prescribed in the various text-books are as diverse as they are numerous, but the general consensus of opinion seems to indicate a strongly acid solution, and in some cases the presence of acetic acid; others, however, advise the use of alkalies, such as sodium carbonate. In considering these methods, it must, of course, be borne in mind that some are well suited to the preparation of the aldehydes or ketones in a state of purity, whilst others are better adapted for their estimation. The latter is the question which the present communication more particularly deals with.

The change which takes place with bisulphite of soda or potash is indicated by the following general equation:—

$$RCHO + NaHSO_3 = RCH\begin{matrix}OH\\SO_3Na\end{matrix}$$

2. By a condensation product formed with cyanacetic acid in the presence of potassium hydroxide. The reaction that takes place for aldehydes is as follows:—

$$RCHO + CH_2CN.COOH = RCH:C\begin{matrix}CN\\COOH\end{matrix} + H_2O.$$

3. By shaking the oil with a saturated solution of sodium salicylate. There seems to be evidence of the formation of a weak molecular compound, and with cinnamic aldehyde well-defined crystals have been obtained which give on analysis:—

No.	*Found.*	*Theoretical.*
7. Sodium	7·3 . .	7·9
11. Sodium salicylate . .	53·5 . .	54·8

4. *Titration Method.*—By treating aldehydes or ketones with an alcoholic solution of hydroxylamine-hydrochloride, when oximes are formed, advantage being taken of the fact that the unused hydroxylamine may be easily titrated back. The reaction is shown in the following equation :—

$$RCHO + H_2NOH = RCH \cdot NOH + H_2O.$$

5. *Another Method, recently suggested by Hanus, for Cinnamic Aldehyde.*—By treatment with an aqueous solution of semioxamazide, when a crystalline semioxamazone is formed, which is filtered off, dried and weighed.

6. The method to which particular attention is now directed, and which gives accurate results with nearly all aldehydes and ketones generally met with, is carried out by heating the oil containing aldehydes or ketones with a neutral saturated solution of sodium sulphite, a soluble sulphonate being formed. In the case of citral the following reaction takes place :—

$$C_9H_{15}CHO + 2Na_2SO_3 + 2H_2O = C_9H_{17}(NaSO_3)_2CH \cdot OH \cdot SO_3 \cdot Na + 3NaOH.$$

Advantage is taken of the fact that an alkali is quantitatively liberated, and may, by adding an indicator such as phenolphthalein, be used to determine the end of the reaction.

The details for using the first three methods can be found in various memoirs, and a description of the same as particularly applied to the estimation of citral is given in the *Journal of S. C. I.*, December, 1901. Since that date the sulphite method has been further investigated, and found to apply equally well to most of the essential oils containing either aldehydes or ketones.

The objections to the use of methods Nos. 1, 2, 3, 4 and 5 are :—

1. The very long time required for shaking ; the difficulty of determining when all the aldehydes are combined; the impossibility of reading the meniscus with accuracy, owing to

the insoluble crystalline mass, often accompanied with resinous bodies, floating at the division of the liquids.

2. This method invariably gives too high results, especially with oils containing high percentages; no clear meniscus is formed.

3. Oils containing different percentages of aldehydes and ketones require different treatment with regard to the quantity of hydroxylamine and bicarbonate of soda required, and no definite instructions for the use of the process can be prescribed, which will apply to all oils.

Substance.	Weight taken.	Bicarbonate Soda.	Mol. Bicarbonate.	Hydroxylamine taken = c.c. $\frac{N}{10}$ NaOH.	Hydroxylamine used.	Time of Heating (minutes).	Percentage.
Benzaldehyde .	1·034	0·4	0·5	124	91	30	93·3
,, .	1·039	0·8	1·0	124	94	30	95·9
,, .	1·037	0·8	1·0	378	85	60	86·9
,, .	0·935	1·1	1·5	378	79	30	89·6
,, .	0·900	1·0	1·5	150	75	60	88·3
Carvone . .	1·411	0·8	1·0	378	90	30	95·7
,, . .	1·410	0·8	1·0	378	83	60	88·9
,, . .	1·408	1·1	1·3	378	89	30	94·8
,, . .	1·346	1·0	1·3	150	80	60	89·2
Caraway oil . .	2·135	1·0	—	150	78	60	54·8
Citronellal . .	1·276	0·35	0·5	124	40	30	48·3
,, . .	1·308	0·7	1·0	124	61	30	71·8
,, . .	1·320	1·1	1·5	378	50	30	58·3
Cuminic aldehyde	1·442	0·4	0·5	124	91	30	93·4
,,	1·459	0·8	1·0	124	98	30	94·3

4. The objection to this method lies in the fact that not only aldehydes, but nearly all oxygenated constituents, are absorbed by this reagent; but it will give, under definite conditions, figures of considerable value in essential oils containing mixtures of alcohol, esters, and aldehydes with terpenes, which will apply to all cases.

Estimation in Essential Oils by the Sulphite Method.—With regard to the determination of aldehydes and ketones, essential oils may be conveniently divided into two classes—

those in which the estimation is made directly on the oil, and those in which the amount is too small to allow of direct estimation, but where preliminary concentration is necessary, such as citron, lime, lemon and orange oils. In cases in which direct estimation on the oil is possible, the procedure is as follows: 5 c.c. of the oil are introduced into a 200 c.c. flask, having a neck graduated to 5 c.c. in $\frac{1}{10}$th of a c.c., with a side tubulus reaching to the bottom of the flask for introducing the oil, reagents and water. To the measured oil is added a saturated solution of neutral sulphite of soda and two drops of ordinary phenolphthalein solution; it is then placed in a water bath and thoroughly shaken, when a red colour is quickly produced. It is carefully neutralised with 1 to 10 solution of acetic acid until, after the addition of a few drops of acid, no further colour is produced. The oil is then run up into the graduated neck, and when cold carefully read. The difference between 5 c.c. and the reading will give the amount absorbed, and this multiplied by 20 the percentage.

The following are results obtained by this process; in each case the substance has been further carefully examined, both chemically and physically, and in all cases represents a pure or commercially pure article.

Aldehydes, Ketones and Oils on which a Direct Determination can be made.

Oil of Almonds (*Bitter*).—The method answers well in the case of this oil.

Benzaldehyde.—The chief constituent of oil of almonds is completely absorbed, even in the cold, giving a clear solution. Experiments made on a mixture of pure benzaldehyde and limonene which had been carefully redistilled over sodium several times gave theoretical results.

Reaction seems to take place according to the following equation:—

$$C_6H_5CHO + Na_2SO_3 + H_2O$$
$$106$$
$$= C_6H_5CH \cdot \begin{matrix} OH \\ SO_3Na \end{matrix} + NaOH$$
$$40$$

The following data are confirmatory:—

Took 5·3 grammes benzaldehyde and 12·6 grammes of crystallised sodium sulphite (theoretical amount) and titrated with N acid. Required:—

Exp.	*NaOH.*	*Calc.*
1 . .	44·2 c.c. = 1·8 grammes . . .	2·0
2 . .	45·6 „ = 1·82 „ . . .	2·0

Well-defined crystals are formed in the neutralised solution on standing. On examination they proved to be identical with the ordinary bisulphite addition product, as the aldehyde is again liberated by the addition of acids or alkalies.

Anisal.—Gives theoretical results and a clear solution. Mixtures of pure aldehyde and limonene gave theoretical results.

Caraway Oil.—The method will be found very useful for this oil, the only convenient test for the valuation of the oil up to the present being its specific gravity, from which is calculated the percentage of carvone present, on the assumption that the oil only consists of limonene and carvone. But this is not sufficient to detect adulteration.

Carvone, as may be inferred from the above, is readily absorbed by this reagent, giving theoretical results. A similar reaction to that which occurs in the case of benzaldehyde probably takes place with this ketone:—

$$C_9H_{14}CO + Na_2SO_3 + H_2O$$
$$150$$
$$= C_9H_{14}C\begin{matrix} OH \\ SO_3Na \end{matrix} + NaOH$$

Took 7·5 grammes carvone and titrated with N acid. Required: 49·4 c.c. = 1·98. Calculated 2·0 grammes NaOH.

Cassia and cinnamon oils both give good results. Large amount of phenolphthalein required.

Cinnamic aldehyde, the chief constituent of the above oils, also gives theoretical results. The following equation probably shows the reaction that here takes place:—

$$\underset{132}{C_6H_5 . CH : CHCHO} + 2Na_2SO_3 + 2H_2O$$

$$= C_6H_5 . CHSO_3Na . CHOH . CH\begin{matrix}OH \\ SO_3Na\end{matrix} + 2NaOH$$

Took 3·3 grammes of aldehyde. Required 46·5 c.c. N acid = 1·86 NaOH. Calculated 2·0 grammes. The same reaction probably applies in the case of citral and citronellal and all olefinic aldehydes.

Citral.—As has been shown elsewhere, the method answers well, giving theoretical results.

Citronellal forms a milky solution, and at first is very frothy. Consequently care must be taken that none is lost through this cause. The reaction takes a considerable time and heating to complete the reaction, but gives good results.

Oil of Cumin.—Litmus solution will be found a better indicator for this oil. A genuine oil gave 24 per cent. cumic aldehyde.

Cumic aldehyde at first forms a solid compound, but on heating with the addition of acetic acid goes into a clear solution. Litmus should be used.

Oil of Dill.—In the case of this oil the method will be found extremely useful, as the carvone may be estimated with accuracy.

Oil of Lemon-grass.—The method with this oil works remarkably well, giving a sharply defined meniscus. It has been shown by Parry that acetone is sometimes added to make the oil pass the solubility test. This would also show as aldehyde by the absorption method. Shaking the oil with

water, or determination of its refractive index, will, however, at once indicate oils thus sophisticated.

Oil of Pennyroyal.—With this oil phenolphthalein does not act well as an indicator. Litmus is better. A recent oil gave 16 per cent. pulegone.

Pulegone.—This gives theoretical results.

Oil of Spearmint.—The method is valuable in the case of this oil and works well, giving a clear solution. Genuine oils give about 62 per cent. carvone.

Oils of Tansy, Thuja and Wormwood.—The method is useless for these oils, for the reason that thujone, the active constituent of these oils, does not form a compound with the reagent.

Nonyl and Decyl Aldehydes.—Considerable time and heating are required to complete the reaction with these substances, but good results may be obtained.

Oils in which a Direct Estimation of Aldehydes and Ketones cannot be made.—In this class there are only four of importance—*viz.*, citron or cedrat, lemon, hand-pressed lime and orange oils; and it will be convenient to consider the estimation of citral in lemon oil first, as the same method and remarks will apply in many respects to the other three oils.

Lemon Oil.—As this oil contains only a small percentage of total aldehydes, and consists chiefly of the inodorous hydrocarbon limonene, it is necessary to carefully fractionate out the hydrocarbons, and, while doing this, the analyst may come to a more definite knowledge of the genuineness of the oil if the following procedure be adopted.

The method, as particularly applied to lemon oil, was first suggested in a paper read before the Society of Chemical Industry in December, 1901, and since that time has been further investigated as a general method for other oils of a similar type, and for convenience is again described.

Having first determined the specific gravity at 15° C., the rotation in a 100 mm. tube by sodium light, and the refractive index at 20° C., the oil is next distilled, and this, if carried out carefully, will show any adulteration. One hundred c.c. of the oil to be examined are put into a distilling-flask having three bulbs blown in the neck, and fitted with cork and thermometer. This is connected to a condenser with a suitable receiver, having two vessels graduated at 10 c.c. and 80 c.c. respectively. A Brühl's apparatus answers the purpose very well. The whole is exhausted, and a pressure of not more than 15 mm. should be obtained. The flask is now gently heated by means of an oil bath, and 10 c.c. distilled into the first tube. The next vessel is then put into position and the distillation continued until 80 c.c. have distilled over. The pressure is now relieved, and the residual oil in the flask distilled over with steam. The quantity so obtained should be carefully noted. Then the differences in rotation and refractive index of fraction 1 and those of the original oil will indicate added turpentine; fraction 2, lemon terpenes; fraction 3, the total amount of oxygenated constituents—*i.e.*, terpeneless oil and the amount of aldehydes.

The aldehyde should be estimated on this fraction after the above two constants have been taken in exactly the same manner as previously described. For example, supposing 7 c.c. of oil were obtained for the third fraction, and that, of the 5 c.c., 2·1 c.c. were absorbed in the aldehyde determination, the percentage of citral in the original oil would be $\frac{2{\cdot}1 \times 20 \times 7}{100} = 2{\cdot}9$ per cent. A few remarks here as to the percentage of citral contained in lemon oil may not be out of place, especially as the subject is one that has recently been the cause of dispute among several essential oil analysts.

The percentage given by this method is somewhere about 3 per cent. for genuine oils, whereas, up to some four years ago,

7 to 7·5 per cent. was the only figure that could be recognised as compatible with a genuine oil.

This higher percentage is still maintained by some analysts, both English and Italian, although there is no known method that will give directly or indirectly a figure anywhere approaching this percentage. The facts admitted on all sides are :—

1. That a genuine oil does not yield more than from 5 to 6 per cent. of concentrated, *i.e.*, terpeneless, oil.

2. The oxygenated constituents in the 90 per cent. or so of terpenes distilled are less than 1 per cent.

3. A concentrated oil never contains more than 50 per cent. of aldehydes, the average being 46 per cent.

On the face of these facts, admitted by all experts, it seems inconceivable that any analyst should maintain a 7 per cent. standard, as, taking an oil yielding at the highest 6 per cent. of concentrated oil, only half or 3 per cent. of this would be of an aldehydic nature.

Such guaranteed 7 per cent. oils must, of necessity, be very misleading to consumers and manufacturers, and tend to place the analysts in a very false position, as on such certificate a manufacturer of concentrated oils would expect a yield of 12 per cent. at least of terpeneless oil; but, as above mentioned, this is not the case.

Hand-pressed Lime Oil.—The method as above described for lemon oils is equally useful for the determination of citral in this oil, which should contain about 8 per cent. of this constituent.

This distillation method would at once show the addition of lemon or orange oil.

Citron or Cedrat Oil.—Consists chiefly of citral and limonene (*vide Analyst*, October, 1901). The same method of distillation may be used. A genuine oil should contain about 4 per cent.

Oil of Orange.—This oil consists chiefly of limonene and a small quantity of decylic aldehyde. The distillation method is useful in detecting adulteration with cheaper oils of the citrus series.

The rotation of the first 10 c.c. should always be higher than that of the original oil, and the aldehydes may be determined on the third fraction. A typical sweet orange oil gives about 0·75 to 1 per cent.

In the processes mentioned above, it must be remembered that the actual results are only approximate. For example, there is a certain small amount of potash used in the ester process, by action on bodies which are not esters but which are readily susceptible to the action of so strong a body as caustic alkali. But the whole of the potash used is calculated to esters, which will, in general, then, be returned a trifle too high. The action of acetic anhydride, too, is powerful, and it is probable that in very few, if in any, cases does the reaction take place in the simple theoretical manner, upon the assumption of which our calculations are based. Again, in absorption processes, errors arise either by secondary reactions taking place, such as when citral is absorbed by bisulphite of sodium solution, or by the incomplete absorption of the absorbable body, or, lastly, by the solution of small quantities of the non-absorbable bodies. In oil of cloves, where the eugenol is estimated by absorption by caustic potash, if the solution of potassium eugenol be separated off and extracted with ether, it is possible to obtain small quantities of the sesquiterpene, caryophyllene, which have been dissolved by the potassium eugenol solution. The reader's attention is drawn to these facts, not with a view to depreciate the value of the processes, which are amongst the most important of all those used in the examination of essential oils, but to accentuate the fact that the estimations of, say, citral in lemon-grass oil, or santalol in santal-wood

oil, are not quite the same thing as the estimation of the majority of inorganic bodies, where determinations can frequently be depended on to $\frac{1}{10}$th per cent.

There are, of course, numerous other quantitative processes having great value in the examination of essential oils, but these will be referred to in the sequel as occasion requires.

CHAPTER V.

SYSTEMATIC STUDY OF THE ESSENTIAL OILS.

Two methods of classification of the essential oils are feasible: either by grouping them according to the identity or relationships of their constituent compounds, or according to the botanical relationships of the plants yielding them. The latter method will be followed in this work, and it will be seen that, although numerous exceptions occur, the oils from plants of the same family very frequently contain the same compound as their preponderating constituent. Probably nearly every odoriferous plant contains an essential oil, in many cases, of course, only in minute quantities, but of course only a limited number have been separated or examined. In the present chapter, the chief of those which have received attention at the hands of chemists will be described, and details of their properties and constituents given as fully as space will allow. The accompanying botanical groups are embraced in this description (p. 143).

OILS OF THE GYMNOSPERMS.

Amongst the numerous families of this widespread natural order, the pines, firs, larches, cedars, cypresses and junipers are perhaps the best known. Most of them yield essential oils from the leaves, fruit and wood, the latter also frequently yielding large quantities of resin. Of these the following are the best known, and many of them are in very common use:—

GYMNOSPERMS - - *Natural Order* - - Coniferæ

ANGIOSPERMS

Monocotyledons

Natural Orders.

- Gramineæ
- Aroideæ
- Liliaceæ
- Iridaceæ
- Zingiberaceæ

Dicotyledons

Natural Orders.

Monochlamydeæ

- Piperaceæ
- Cannabinaceæ
- Myricaceæ
- Salicineæ
- Chenopodiaceæ
- Laurineæ
- Myristiceæ
- Euphorbiaceæ
- Cupuliferæ
- Santalaceæ

Gamopetalæ

- Labiatæ
- Verbenaceæ
- Convolvulaceæ
- Jasmineæ
- Ericaceæ
- Valerianeæ
- Compositæ
- Caprifoliaceæ

Polypetalæ

- Umbelliferæ
- Myrtaceæ
- Rosaceæ
- Leguminosæ
- Saxifragaceæ
- Hamamelideæ
- Terebinthaceæ
- Geraniaceæ
- Tropæoleæ
- Rutaceæ
- Zygophylleæ
- Anacardiaceæ
- Burseraceæ
- Tiliaceæ
- Malvaceæ
- Ternstrœmiaceæ
- Clusiaceæ
- Dipterocarpeæ
- Polygalaceæ
- Cruciferæ
- Resedaceæ
- Turneraceæ
- Cistineæ
- Ranunculaceæ
- Magnoliaceæ
- Anonaceæ

I. Wood Oils.

Cedar Oil.—The oil usually known as cedar oil or cedar-wood oil is obtained by distillation of the wood of *Juniperus virginiana*, the Virginia cedar, one of the family of the *Cupressineæ*. Other cedar-wood oils are occasionally met with, and will be mentioned later, but the present remarks apply to the above-mentioned oil.

The oil is generally distilled from the waste shavings from lead pencil manufacture, which are usually plentiful when the pencils are cut from logs. When thin sawn boards are imported and used, the refuse is much smaller in amount, and the price naturally rises. The yield of oil obtained varies from 2·5 to 5 per cent. *Juniperus virginiana* occurs over a very wide area in America, and some of the finest oil is obtained from the Florida cedar. This oil is one of those oils which is indispensable in certain classes of perfumery, especially in fine soap-making, where intensely "sweet" odours are not required. The wood in fine powder finds its way into much of the incense and similar preparations used either for ceremonial or fumigating purposes.

The oil is usually of a brownish colour, but it can be obtained almost water white, and although we know nothing definitely of what change occurs, it is certainly amongst those oils which improve in quality by keeping.

Pure cedar-wood oil has a specific gravity of from ·940 to ·960, and is always laevo-rotary. The limits, however, are wide, the oil varying from − 25° to − 40°. According to Schimmel, 80 per cent. distils at between 125° and 155° at a pressure of 14 mm. The refractive index is very high, usually exceeding 1·5, and often rising to 1·51. It is very insoluble in alcohol, 1 part requiring 10 to 20 parts of 90 per cent. alcohol for solution. The known constituents of the oil are the sesquiterpene cedrene, $C_{15}H_{24}$, and the oxygenated body

cedar camphor, or cedrol, $C_{15}H_{26}O$. The former body has already been referred to. The latter, when pure, is a silky crystalline mass, with pleasant aromatic odour, melting at about 78° to 80°. It is suggested by Schimmel that cedrol is not a normal constituent of fresh wood, but is formed in it by keeping it under favourable conditions. This supposition has not, however, been experimentally justified except in so far as very old wood yields a semi-solid oil, which deposits much cedrol on cooling. At all events, only a small quantity occurs in normal oils, as is shown by the low acetylation figure. If the oil be acted upon by acetic anhydride, and the resulting product saponified, no more than from 6 to 8 per cent. of cedrol will be indicated. It must be remembered, however, that dehydration takes place to a small extent with acetic anhydride, so that the result may be somewhat underestimated. Ten per cent. may be regarded as the maximum usually occurring in good oils. The figures found by the author for four pure samples (percentage of KOH to saponify the acetylated oils) are as follows: 2·32, 2·21, 2·13, 1·72.

For further details of the chemistry of the oil, reference should be made to a paper by Rousett (*Bull. de la Soc. Chem.*, 1897, p. 485). In some of the American pencil factories an inferior oil is obtained by condensing the vapours obtained from the drying chambers, but this oil is of very indifferent odour and not much used.

Oil of Jamaica cedar or Honduras cedar is distilled from the wood of *Cedrela odorata*, a West Indian plant of an entirely different family. This oil is more correctly termed cedrela-wood oil, and will be referred to later. Other cedar oils, which have a right to the name, are the following. From *Cedrus Libani*, the enormous tree found in Lebanon and Taurus, and now a favourite in English grounds; this is a brown oil of specific gravity about ·980 and laevo-rotary

– 10° to – 20°. From *Juniperus Bermudiana;* this is a light-coloured and pleasant-smelling oil.

Corinto cedar-wood oil has a specific gravity of about ·906 and is laevo-rotary. Its botanical origin is uncertain. A Cuban oil, also of uncertain origin, is dextro-rotary, and contains cadinene, and a La Plata oil is optically inactive. An oil from Punta-Arenas is slightly laevo-rotary, of low specific gravity, and contains cadinene. These oils, of uncertain botanical origin, however, are of little commercial importance.

Pure cedar oil is fairly cheap, varying in price (as obtainable from wholesale houses) from 1s. 9d. to 4s., or thereabouts, per lb., according to quality. Hence it is not much adulterated. It is employed, however, to adulterate other oils, notably santal-wood oil, and formerly also patchouli oil.

Hayti cedar-wood oil is derived from an unknown source. Its specific gravity is 0·961 and rotation – 15°. It contains about three times more alcoholic bodies than the ordinary cedar oil. It also contains a very small amount of free acids and of esters.

Quite recently an oil has been distilled which has attracted some attention, as it is said to have a therapeutic value in urinary complaints. This is the oil from *Cedrus Atlantica*, a variety of *Cedrus Libani*. The oil has a specific gravity 0·951, refractive index 1·5119, and optical rotation + 60° 32′. It contains about 16 per cent. of alcoholic bodies. It owes its peculiar odour to the presence of a ketone $C_9H_{14}O$, which has been termed libanone, and which yields a semicarbazone melting at 159° to 160°. From the oil was also separated dextro-cadinene, having a specific gravity 0·9212, optical rotation + 48°, and refractive index 1·5094.

Oil of Turpentine.—Numerous members of the family of the *Coniferæ* contain large quantities of resin, and an oil con-

sisting almost entirely of terpenes, in well-characterised resin ducts in the wood. This is especially the case with the various species of pine. The exudation from the wood, an oleo-resin, is often known as crude turpentine. Oil of turpentine, or, as it is generally called, turpentine or "turps," is the oil obtained by distilling this, leaving the crude resin or "rosin" behind. Before mentioning the chief varieties of turpentine, it will be convenient to briefly describe the process by which it is obtained, for example, in the United States. Here the principal source of the oil is *Pinus Australis*, usually known locally as the yellow or Georgia pine. During the autumn and winter months the trees are "boxed". This operation consists in making excavations of characteristic shape into the trunks of the trees, about six to eight inches above the roots. These excavations or "boxes" are made so as to hold from one-half to one gallon, and in a day or two after they have been made, the trees are barked to the height of about three feet above the box, and some of the wood is also scraped off and hacks are made in the wood to allow the crude oleoresin to exude into the boxes. This exudation commences about March, and runs to the end of August, and, somewhat more slowly, during the next month or two. The crude turpentine is then baled out into rough barrels. As a rule, the trees are hardly worth treating for more than five or six years, as the oleoresin then yields little oil. Occasionally great exceptions to this rule are found. The crude turpentine is transferred to stills and subjected to a temperature of about 140° C., until the little water and volatile impurities present are driven off. Water is then added to the still, and the turpentine oil is distilled and separated from the watery layer. It is transferred to oak barrels holding about three hundredweight, in which packages it is exported. These barrels are very well made, and when empty are always worth about four shillings. Turpentine is

a colourless liquid when pure, but easily resinifies and darkens on exposure to the air. It has a somewhat unpleasant odour, and is not used for perfumery purposes at all, but it finds very extensive employment as a solvent, and vehicle in the manufacture of varnishes and paints. It is also used for the manufacture of medicinal terebene, and, to a certain extent, for other pharmaceutical and medicinal purposes.

The following are the best-known varieties of oil of turpentine:—

American Turpentine.—This is chiefly obtained from *Pinus Australis*, but also to a certain extent from *Pinus taeda*, the loblolly pine. It is a colourless limpid liquid of specific gravity ·855 to 870. It used to be invariably dextro-rotary, to the extent of about + 10° to + 15°, but is now usually found with a dextro-rotation of + 1° to + 5°, and often it is slightly laevo-rotary. This alteration is due to the extension of the gathering grounds and possibly to some differences in the method of collection. It commences to boil at 156° to 157°, and in good samples 88 to 99 per cent. will distil below 165°. Its chief constituent is pinene $C_{10}H_{16}$, and a little dipentene is also present. Its refractive index is from 1·4700 to 1·4730 at 20° C.

French Oil of Turpentine.—This variety is chiefly obtained from the oleoresin of *Pinus pinaster*. Here again the chief constituent is the terpene pinene, and the great difference between this and American turpentine lies in the fact that the former is laevo-rotary, about − 18° to − 40°.

German Oil of Turpentine is chiefly the product of *Pinus sylvestris*, but *Pinus abies*, *Pinus vulgaris* and *Pinus picea* also contribute to it. Its specific gravity is ·860 to ·870, and it is dextro-rotary, about + 15° to + 20°. It contains pinene and sylvestrene.

Russian and Swedish Oil of Turpentine.—This variety

is almost entirely obtained from *Pinus sylvestris* and *Pinus ledebourdii*. In general properties it resembles German oil, but it is rather more variable in specific gravity, etc. According to Tilden, it contains as much as 60 to 70 per cent. of sylvestrene. Its specific gravity is usually about ·870 to ·875, and its boiling point about 170°. It is dextro-rotary to the extent of + 20°. Of all the commercial turpentines it is of the least technical importance. It often possesses a disagreeable empyreumatic odour, due to the presence of the products of destructive distillation of the pine-wood.

Indian Turpentine.—This turpentine, distilled from *Pinus longifolia*, has a specific gravity 0·8741, rotation + 0° 43′ and distils between 165° and 180° to the extent of 80 per cent.

Grecian Turpentine.—This oil is distilled from *Pinus halepensis*. It has a specific gravity 0·8634, rotation + 77° 34 and refractive index 1·4678. It distils between 150° and 155°.

Other less important turpentines are Hungarian (from *Pinus pumilio*); Austrian (from *Pinus laricio*); Carpathian (from *Pinus cembra*), and Finnish (similar to German). In addition, Venetian turpentine and Canada balsam yield oils. These latter, however, have practically no commercial interest.

The terebene of pharmacy consists of optically inactive terpenes, the result of the action of sulphuric acid on turpentine, which causes a certain amount of isomerisation, and also changes the active terpenes into their inactive variety. For the manufacture of this, it is preferable to employ rectified oil of turpentine. Indeed, for pharmaceutical purposes in general, it is usual to employ turpentine purified by redistillation.

Turpentine is sometimes adulterated with petroleum and with rosin spirit, and with so-called pine-tar oil (often known as pinolin), and, rarely, with volatile portions of shale oil and

coal tar. It is itself used very largely to adulterate other essential oils, both on account of its price and because it so closely resembles many other oils in chemical constitution.

The accompanying table (p. 151) is given by Allen (*Commercial Organic Analysis*), embracing certain properties of these bodies.

The chief points of importance to be noted in the examination of the oil are the specific gravity, boiling point and temperature of distillation, optical activity, refractive index and flashing point. The characters of the fractional distillates should be examined.

Good commercial turpentine has a specific gravity of ·858 to ·870, only occasionally passing these limits slightly. Russian oil has a higher gravity—often reaching ·875. The optical activity, as stated above, varies with the source, and this factor is only of value when studied in conjunction with the other features of the oil. The boiling point is usually 155° to 156°, and a considerable portion distils at below 160°. In the best class of oils at least 85 per cent. distils below 165°, often several degrees below this temperature. Russian oil, on the other hand, distils chiefly between 170° and 180°. When adulterated, the temperature of distillation rises gradually, and no large fractions are obtained at any definite temperature when the adulteration is at all excessive. The presence of ordinary petroleum spirit lowers the flash point of turpentine. When pure, it flashes at 92° to 95° F. when tested in Abel's flash point apparatus. With only 1 per cent. of ordinary petroleum spirit this temperature is reduced by 10°.

According to Armstrong, a good indication of the presence of the usual adulterants is obtained by distillation with steam. A current of steam is allowed to pass into a definite volume of the turpentine contained in a flask attached to a condenser. Unless it has been allowed free access to the air for some time,

	Turpentine Oil.	Rosin Spirit.	Petroleum Naphtha.	Shale Naphtha.	Coal-tar Solvent Naphtha.
1. Optical activity . . .	active	usually none	none	none	none
2. Specific gravity . . .	·860-·872	·856-·880	·700-·740	·700-·750	·860-·875
3. Temperature of distillation .	156°-180°	gradual rise	gradual rise	gradual rise	gradual rise
4. Action in the cold on coal-tar pitch	readily dissolves	readily dissolves	very slight action	very slight action	readily dissolves
5. Behaviour with absolute phenol at 20° . . .	homogeneous mixture	homogeneous mixture	no apparent solution	homogeneous mixture, crystallises on cooling	homogeneous mixture
6. Behaviour on agitating 3 vols. with 1 vol. castor oil . .	homogeneous mixture	homogeneous mixture	two layers of nearly equal volume	like petroleum naphtha	——
7. Bromine absorption (dry) .	203-236	184-203	10-20	60-80	——
8. Behaviour with H_2SO_4 . .	almost entirely polymerised	polymerised	very little action	considerable action	moderate action

the genuine oil leaves only traces of non-volatile matter, but old samples may leave up to 2 per cent. Usually, however, the presence of more than ·5 per cent. after steam distillation indicates the presence of unvolatilised petroleum oil. This is easily recognised by its low specific gravity and its fluorescence when dissolved in ether. If the residue consists of resin oil, it will form a bulky soap when rubbed with slaked lime. The specific gravity of the fractions coming over with the steam will largely assist in determining the presence of volatile adulterants.

For the approximate estimation of the amount of petroleum naphtha in adulterated turpentine, Armstrong recommends the following process: 500 c.c. of the sample is placed in a separator and treated with about 150 c.c. of sulphuric acid (two volumes of acid to one of water). The mixture is cautiously agitated, and, if much rise of temperature is observed, the separator must be placed in cold water for a short time. The turpentine is gradually converted into a viscid oil, and when this has taken place, and no more heat is developed on repeated agitation, the acid is tapped off. The oily layer is then transferred to a flask and subjected to steam distillation. When all that is volatile with steam has passed over, the oily portion of the distillate is separated from the aqueous layer, and heated with half its volume of sulphuric acid previously diluted with one-fourth of its measure of water. The mixture is well agitated, the acid liquid separated, and the oily layer again distilled with steam. When genuine turpentine is operated upon, the volatile portion of this second treatment consists merely of cymene and a small quantity of paraffinoid hydrocarbons. It never exceeds 4 to 5 per cent. of the volume of the original sample, and with care is as low as 3 per cent. If the volume notably exceeds 5 per cent., it is advisable as a precaution to repeat the treatment with the (4 to 1) acid. When treated in this

manner, petroleum naphtha is not appreciably affected, hence the proportion may be fairly estimated by making an allowance of 4 to 5 per cent. from the volume of volatile oil which has survived the repeated treatment with sulphuric acid. A further purification may be effected by violently agitating the surviving oil with several times its volume of concentrated sulphuric acid heated to 50° or 60°. This treatment can be repeated if necessary, after which the residual hydrocarbon is separated, steam distilled, and again measured, when the surviving oil from pure turpentine oil will not exceed from ½ to 1 per cent. of the original sample. Any excess over this will be the minimum quantity of petroleum naphtha present. Shale naphtha cannot be at all estimated in this way. The behaviour of the oil on distillation is the best indication of the presence of rosin spirit, as the temperature rises gradually, and no considerable fraction is obtained at 158° to 160° if much rosin spirit be present.

In his studies on the use of dimethyl sulphate for the detection and the estimation of tar oils in mixtures with resin oil and mineral oil, E. Valenta has observed the behaviour of dimethyl sulphate towards fatty oils, turpentine oil and pinolin. Pinolin and turpentine oil, when shaken with equal parts of dimethyl sulphate, cause an increase in the volume of the layer of dimethyl sulphate, as about 30 per cent. of both are dissolved. Pinolin imparts an orange colour to the mixture; pure turpentine oil does not colour it, but a mixture of turpentine oil and dimethyl sulphate causes a large increase in the temperature, whilst pinolin with dimethyl sulphate produces a scarcely perceptible rise in temperature. The author believes that these reactions can be employed with advantage in testing turpentine oil for pinolin.

According to Valenta, pine-tar oils have all a higher refractive power than pure oils of turpentine, as it is usually found above 1·471, a figure which pure turpentine

oils seldom reach. As a distinguishing reaction between pine-tar oil and turpentine oil, Valenta mentions the following: if equal volumes of 1 per cent. gold chloride solution and oil of turpentine are shaken in a test tube and placed on the water bath, heated for one minute, and the test tube is then removed and shaken, pure turpentine oils only show a separation of gold in the oil film. The solution itself does not become discoloured. Pine-tar oil discolours the gold solution completely.

For the purpose of distinguishing turpentine oil from pine-tar oil, the reaction observed by Herzfeld (shaking equal volumes of oil and a solution of sulphurous acid, when the layer of oil, in the presence of pine-tar oil, acquires a yellowish green colour) is useful. Utz also employs for this purpose the following reaction: equal volumes of the oil and of solution of stannous chloride are mixed. In the case of Austrian turpentine oil the reagent became yellow, the oil colourless; with Greek, the reagent orange, the oil yellow, and with American turpentine oil the reagent orange and the oil yellow. The solution of stannous chloride acquires with pine-tar oil a red colour; the oil remains yellow, but in many cases the oil itself also coloured red. The reaction also takes place in mixtures of pine-tar oil with turpentine oil.

The *British Pharmacopœia* (1898), in which turpentine is official, requires it to be soluble in an equal volume of glacial acetic acid, and to boil between 160° and 180°.

It is to be remembered that the determination of the refractive index is of the greatest importance in testing oil of turpentine.

Juniper-wood Oil.—It is said that a volatile oil is obtained by distilling the wood of *Juniperus communis* with steam, but commercial juniper-wood oil is merely turpentine distilled over juniper-wood, or more usually a mixture of juniper berry oil and turpentine. So-called juniper-wood oil, however,

finds a certain amount of employment as a cheap substitute for the oil of juniper berries. By the distinctive distillation of the wood of *Juniperus oxycedrus*, an empyreumatic oil known as oil of cade (*Oleum cadinum; huile de cade*) is obtained. This is a dark-brown tarry liquid of empyreumatic odour, employed in the treatment of certain skin diseases. Its principal constituent is cadinene, but as it is not one of the essential oils proper it need not be further discussed here.

II. Fruit Oils.

The most important oils obtained from the fruit of coniferous trees are juniper (from berries of *Juniperus communis*) and fir cone oil (from cones of *Abies pectinata*).

Juniper Berry Oil.—The plant yielding this oil is *Juniperus communis*, a native of Greece, and widely distributed over Europe. It is a small shrub or tree varying from two to six feet in height, but in parts of Norway it forms a forest tree some thirty to forty feet in height. The Italian berries, however, are most valued for oil. According to Pereira, the juniper of the Bible was a leguminous plant, probably the broom or furze tree. Fraas considers the *κέδρος μικρα* of Dioscorides was our juniper. The plant is usually dicœcious, and the scales of the cones, when ripe, become succulent, and cohere to form a kind of berry (galbulus). These berries are rich in sugar, and by their fermentation and distillation the well-known beverage, gin, is obtained, which owes its characteristic flavour to the oil of juniper. The *British Pharmacopœia* states that the oil is distilled from the full-grown unripe fruit. But with reference to this point, Schimmel (*Report*, October, 1898, p. 30) states that "this is an error, at least no such oil is distilled on a large scale. It is an antiquated idea, originating with Zeller, that unripe fruits render a larger yield in oil than ripe ones. In any case, the

oil distilled from unripe berries in all essential qualities is inferior to normal oil of ripe fruits." The following are given by Schimmel as the average yields of oil from plants grown in certain districts :—

Bavarian .	1·2 per cent.	Italian .	1 to 1·5 per cent.
East Prussian	·6 per cent.	Polish . .	·9 per cent.
Thuringian .	·7 per cent.	Hungarian	·8 to 1 per cent.
Swedish .	·5 per cent.		

The only constituents of oil of juniper which have been ascertained with certainty are (1) the terpene, pinene $C_{10}H_{16}$; (2) the sesquiterpene, cadinene $C_{15}H_{24}$; (3) juniper camphor, a crystalline body probably belonging to the series of terpene alcohols. According to Schimmel, the chief, if not only, constituent of the stearoptene is a sesquiterpene alcohol melting at 165° to 166° ; (4) and a small amount of esters not yet fully investigated, but of which the principal one is an ester boiling at about 180°, probably the acetic ester of the above-mentioned alcohol.

The *British Pharmacopœia* demands that the specific gravity of the oil should lie between ·865 and ·890, and that it should be soluble in 4 volumes of 95 per cent. alcohol. The age of the berries from which the oil is distilled produces a marked effect on the specific gravity of the oil, as does also the time for which the latter has been kept, as exposure to the air causes gradual resinification. The solubility also decreases when the oil is kept. Rectification also naturally alters the specific gravity, which depends chiefly on the relative proportions of terpene (sp. gr. = ·860) and sesquiterpene (sp. gr. = ·920). The limits ·865 and ·900 are certainly those which should be accepted for genuine, good oils. Its refractive index is from 1·4740 to 1·4880. The approximate proportions of pinene and cadinene may be judged by a fractional distillation, as pinene boils at 156° and cadinene at 274°. The results vary largely according to

the fractionating apparatus used, but with a series of bulbs, from 25 to 35 per cent. is obtained between 155° and 160°, and from 10 to 20 per cent. between 270° and 280°. The oil is nearly always laevo-rotary, never exceeding − 12°, usually, in the author's experience, from − 4° to − 6°. It is rarely slightly laevo-rotary. With our present knowledge of this oil, no further analytical methods are yet available. Hungarian juniper berry oil is often laevo-rotary to the extent of − 18°. A good juniper oil should contain sufficient cadinene for the residue after distilling off 80 per cent. to have a refractive index of 1·4900.

Juniper oil is of considerable commercial importance. It is employed largely in the manufacture of artificial gin, which is a spirituous solution which is not obtained by the fermentation of the berries. Indeed, essence of gin, which is chiefly, if not entirely a solution of the oil in alcohol, is a regular commercial article. The oil is also employed in medicine, as a sudorific and diuretic. The berries are imported from various European ports, in bags and barrels, but the Italian berries are preferred to all others. The importation in bags is becoming less common, as the berries are very liable to be bruised, when fermentation may set in.

The oil from the berries of *Juniperus Phœnicea*, from Smyrna, has been examined by Schimmel. The berries, which are bright red, yielded 1 per cent. of oil of specific gravity ·859 and optical rotation − 4° 55′. According to Rodié, this oil contains an aldehyde and a considerable quantity of alcohols. The berries of *Juniperus oxycedrus* (Dalmatian) yield an oil of specific gravity ·851 and optical rotation − 8°. The oil from *Juniperus oxycedrus* usually has a specific gravity 0·850 to 0·855 and an optical rotation − 4° to − 9°.

Fir Cone Oil.—This oil, obtained from the young cones of *Abies pectinata* (*Abies excelsa*), is sometimes sold under

the name of pine oil. It contains very little bornyl acetate (the ester characteristic of the fine pine needle oils), never more than 2 per cent., but consists almost entirely of *laevo*-pinene and *laevo*-limonene. Its specific gravity is about ·855 to ·865, and it is laevo-rotary up to − 80°.

The oil from the cones of *Abies alba* has a specific gravity 0·850 to 0·870 and a rotation of − 60° to − 75°. It contains up to 4 per cent. of esters calculated as linalyl acetate, and a large amount of laevo-limonene. That from the cones of *Abies reginæ Amaliæ*, a fir growing in the forests of Arcadia, has a specific gravity 0·868 and a rotation of − 20°. It consists almost entirely of terpenes.

III. Leaf Oils.

Thuja Oil.—This oil is obtained by distillation with steam of the leaves and possibly also the small twigs of *Thuja occidentalis*, the well-known *arbor vitæ*, sometimes also called the white cedar. The yield of oil is from ·5 to 1 per cent. It is almost colourless, but by oxidation becomes slightly greenish or yellow. Its odour is not particularly pleasant, somewhat recalling that of tansy oil. It is frequently adulterated with cedar oil, pine-leaf oils or turpentine, but when pure has a specific gravity of not less than ·910, usually from ·915 to ·925. Its optical activity is given by Schimmel as − 5° to − 14°, but the author has found genuine oil with a little higher rotation than this, so that − 5° to − 15° may be regarded as outside limits. The earliest scientific investigations of this oil are those of Schweizer and Jahns, but that of Wallach, undertaken when our knowledge of the group of compounds contained in the oil was a little more advanced, is now the standard work. The chief constituents of the oil are pinene, *laevo*-fenchone $C_{10}H_{16}O$, and the isomeric ketone, thujone, which also occurs in the oils of tansy, wormwood and sage. Traces of esters,

probably of acetic and formic acid, are also present, and possibly carvone. A small quantity of laevo-borneol or its esters is also present. The highest boiling constituents of the oil have not yet been thoroughly examined, but Wallach believes them to contain the last-named body in the inactive form. A pure oil should have the characteristics mentioned above, *viz.*, specific gravity ·910 to ·925; optical activity $-5°$ to $-15°$; and should be soluble in three times its volume of 70 per cent. alcohol. Thuja oil is not of much commercial importance.

An oil has been obtained from the roots of *Thuja orientalis* with a specific gravity ·979, but little is known of its composition. Its odour resembles thymo-quinone.

Oil of Savin is obtained from the fresh twigs of *Juniperus sabina*. It is an oil which finds but a limited employment in legitimate pharmacy as a uterine stimulant and emmenagogue. It is of no value for perfumery purposes, as its odour is somewhat unpleasant. It is occasionally used for criminal purposes, and one case is recorded of a medical man being sentenced to transportation for having used it with the intention of procuring abortion (*vide Medical Times and Gazette*, 17th April, 1852, p. 404). It was official in the 1885 *British Pharmacopœia*, but it has been wisely omitted from the 1898 edition. The yield of oil from the twigs is fairly high, varying from 3 to 5 per cent., and the oil only fetches a few shillings a pound.

The oil contains a number of constituents, of which Wallach first characterised the sesquiterpene, cadinene. A considerable proportion of terpenes is present, which appear to consist chiefly of pinene with some sabinene. The most recent work on the subject, however, is that of Fromm (*Berichte*, 1898, p. 2025), who separated the oil into three main portions by fractional distillation. The earliest distillate, below 195°, contains furfurol, di-acetyl and methyl alcohol

(Schimmel), but consists mainly of terpenes; the middle portion, 195° to 235°, consists chiefly of ethereal salts, and the last portion, 235° to 310°, consists of cadinene and some resinous bodies, which are possibly the effects of heat on the terpenes. The middle fraction yields an oil boiling at 222° to 224°, which was shown to be the acetate of an alcohol $C_{10}H_{15}OH$, which the author terms sabinol and which is present to the extent of 10 per cent. (Schimmel had previously identified an alcoholic acetate, but the formula of the alcohol was given as $C_{10}H_{17}OH$). The alcohol, obtained by hydrolysing the acetate, is a colourless oil, boiling at 208° to 209°, and with only a faint odour. According to Schimmel (*Report*, October, 1895, p. 44), the amount of this ester present is about 40 per cent., and there is in addition about 10 per cent. of the free alcohol in the oil. There is also present a small amount of either an aldehyde or a ketone boiling between 220° to 250°, yielding a hydrozone melting at 41° and an oxime melting at 85°.

A pure oil, free from turpentine, which is often used to adulterate the French oil, should have a specific gravity of ·910 to ·928, and should be dextro-rotary + 40° to + 60°. Its refractive index is 1·4700 to 1·4770. It should be soluble in its own volume of 90 per cent. alcohol, and should not yield more than 25 to 28 per cent. of distillate below 200°. Its ester number should be between 110 and 130. When a sufficient number of samples have been examined, it may be possible to fix an ester and alcohol limit, but at present it would be unwise to do so.

According to Umney and Bennett, the French savin oil is probably distilled from the leaves and twigs of *Juniperus Phœnicea* which accounts for its difference from the German and English distillates. This French oil has a specific gravity about 0·890; rotation + 4° 30′; esters 9·3 per cent.; total alcohols as sabinol 17·1. Schimmel & Co., on the

other hand, describe the oil from the leaves of this plant as having the following characters: specific gravity, 0·8643; optical rotation, + 7° 20′; ester number, 1·2. They consider that the oil of *Juniperus thurifera* may be used to mix with true savin oil in cases where certain abnormal oils are met with.

Cedar-leaf Oil.—The true cedar-leaf oil may be regarded as the distillate of the leaves of *Juniperus virginiana*, the red cedar, but the confusion implied in the name "cedar" is reflected in the enormous variations met with in commercial samples of so-called cedar-leaf oils. No doubt the leaves of *Thuja occidentalis* and *Chamæcyparis sphæroidea* contribute largely to the commercial oil. Brannt, indeed, describes the oil as having a "penetrating, disagreeable odour," and as "therefore not suitable for perfumery purposes". As a matter of fact, the pure oil has a pleasant, sweet odour, and possesses a specific gravity ·883 to ·888. Its optical rotation varies from + 55° to + 65° (according to Schimmel, + 59° 25′). The examination of a pure sample by Schimmel showed that it contains limonene, cadinene, borneol and bornyl esters, probably including bornyl valerianate; other terpenes are also present. Commercial oils have specific gravities of 0·860 to 0·920 and optical rotations of − 3° to − 24°.

The true *Juniperus virginiana* leaf oil is more expensive than the corresponding oil from cedar-wood—being worth from three to five times as much, in fact, and as the oils from thuja and other leaves are also less costly, it is a matter of importance that the oil should be carefully examined. Six commercial samples and one pure sample, examined by Schimmel & Co., gave the following results:—

	Sp. Gravity.	*Optical Rotation.*	*Solubility in 70 % Alcohol.*
Pure oil .	·887	+ 59° 25′	very insoluble.
1 . .	·897	− 12° 25′	insoluble.
2 . .	·886	− 3° 40′	insoluble.
3 . .	·887	− 24° 10′	insoluble.
4 . .	·920	− 10° 25′	soluble in 4 parts.
5 . .	·918	− 10° 55′	soluble in 5 parts.
6 . .	·905	− 10°	insoluble.

Sequoia Oil is obtained from the leaves of *Sequoia gigantea*, the Californian mammoth tree. Lunge and Steinkauler obtained the oil from smaller ornamental trees grown in Zurich. The first portion of the distillate contained a crystalline hydrocarbon $C_{13}H_{10}$, melting at 105°, which these chemists termed sesquoiene. The later distillate contained a dextro-rotary terpene boiling at 155°, and having a specific gravity 0·852 and optical rotation + 24°, and an oxygenated body $C_{10}H_{20}O_3$. These bodies require further investigation, but as the oil has no commercial importance, it has not attracted much attention so far.

Pine-needle Oil.—There are few oils in commerce in regard to which so much confusion exists as in the case of the so-called pine-needle oil. The oils from the leaves of the *Coniferæ* consist so largely of terpenes that much of the cheap commercial oil consists largely of turpentine, either mixed with a little of the genuine oils, or distilled over pine leaves. We are indebted chiefly to Bertram and Walbaum for a careful investigation of the properties of pure oils of known botanical source. Of these, the following are the most important, known as pine-needle oils. The oil of *Abies pectinata* (*A. excelsa*), distilled from the needles and young shoots of this pine (the Norwegian spruce fir), is perhaps the most valued of all the pine-needle oils. It possesses a fine fragrant odour, and is exceedingly useful for fine perfumery where the best pine odour is required. It has been found to contain *laevo*-pinene, *laevo*-limonene, a

sesquiterpene (possibly cadinene) and *laevo*-bornyl acetate. The latter ester, which is characteristic of the pine odour, occurs to the extent of 4·5 to 7·5 per cent. It is a colourless oil, of specific gravity about ·865 to ·875 and laevo-rotary, according to Schimmel, from – 20° to – 60°. The oil from the young cones of this tree is often sold as pine-needle oil, but it differs from the above-described in containing very little bornyl acetate (*vide supra*).

The oil of *Pinus sylvestris*, the true Scotch fir, was official in the *British Pharmacopœia* in 1885, but has been replaced in the new edition by that of *Pinus pumilio*. The former oil (*P. sylvestris*), distilled from Swedish leaves, and examined by Bertram and Walbaum, had a specific gravity ·872, and was dextro-rotary + 10° 40′. The constituents found were *dextro*-pinene, *dextro*-sylvestrene and bornyl acetate (3·5 per cent.). A fractional distillation showed that 44 per cent. distilled between 160° and 170°, and 40 per cent. between 170° and 185°. A sample distilled by themselves from German-grown trees was also examined by these chemists, and had a specific gravity ·886 and an optical rotation of + 10°; 10 per cent. distilled between 160° and 170°, and 46 per cent. between 170° and 185°. *Dextro*-pinene, *dextro*-sylvestrene, cadinene and probably dipentene and bornyl acetate were found in the oil. Umney has examined a sample distilled by himself from leaves gathered near Sevenoaks, and found it to possess a specific gravity ·8855, and, in contradistinction to Bertram and Walbaum's oil, it was *laevo*-rotary – 19°. About 3·5 per cent. of bornyl acetate was found, and Umney concludes that not more than 15 per cent. should distil below 170°. Taking as criteria the two oils which were actually distilled by these chemists, one may infer that the pure oil from this source should possess a specific gravity of not less than ·880; should not rotate the plane of polarisation more than 20° either to the right or the left (Schimmel has, however, found an

American oil, probably genuine, as high as – 25°), and should not yield a distillate below 170° of more than 15 per cent., nor one between 170° and 185° of less than 40 per cent. It may be noted that the 1885 *Pharmacopœia* allowed so low a gravity as ·870. In order to determine how far the difference in rotary power observed by Bertram and himself could be accounted for by the season at which the leaves were gathered, Umney distilled samples at different times of the year, and, although he found that oil distilled in December was laevo-rotary to the extent of – 7° 45′ as against – 19° for oil distilled in June, he concludes that soil and climate are the chief factors which determine the difference in rotary power. True oil of *Pinus sylvestris* is but rarely found in commerce. The commercial oil is the distillate of various other pines.

The oil of *Pinus pumilio* contains *laevo*-pinene, *laevo*-phellandrene, sylvestrene, cadinene, dipentene and bornyl acetate (4 to 7 per cent.). This oil has a specific gravity of ·865 to ·875, and is laevo-rotary to the extent of – 5° to – 10°. A sample fractionated by Umney gave only 2 per cent. below 165°, and as much as 59 per cent. between 165° and 180°. This oil is official in the present edition of the *British Pharmacopœia*, which demands that its specific gravity should fall between ·865 and ·870, and its optical rotation between – 5° and – 10°. Not more than 10 per cent. is to distil below 165°.

The oil from the needles of *Abies sibirica* is one of the cheapest of the genuine pine-needle oils, and is not held in much favour. Its specific gravity is ·910 to ·920, and it is *laevo*-rotary – 30° to – 45°. It contains up to 30 per cent. of bornyl acetate. Laevo-camphene is present in this oil.

Picea vulgaris needles yield a small amount of an oil of specific gravity ·880 to ·890, laevo-rotary about – 20° containing *laevo*-pinene, *laevo*-phellandrene, dipentene, cadinene and *laevo*-bornyl acetate. The oil from *Pinus picea*

is very similar to this, usually having a specific gravity ·872 to ·876 and an optical rotation of about – 50°. *Abies canadensis* yields the so-called spruce or hemlock spruce oil. This has a specific gravity of about ·905, is *laevo*-rotary about – 20°, and contains *laevo*-pinene, cadinene and *laevo*-bornyl acetate (3·6 per cent.), and also a small amount of camphene.

The oil from *Pinus nigra* is characterised by its containing 50 per cent. of bornyl acetate. Its specific gravity is about ·925 and its rotation – 40°. It was examined by Kremers. A number of other pine-needle oils have been examined, but it is not necessary to devote further space to them; their characteristics are given in the appended table (p. 166).

From a commercial aspect these various pine-needle oils have remarkably different values. There seems but little doubt that the greater part of the *genuine* pine-needle oil of commerce sold as oil of *Pinus sylvestris* is distilled from *Abies pectinata* (*A. excelsa*)—in the author's experience chiefly from the young cones; the true oil of *Pinus sylvestris* is rarely met with. That from *Pinus pumilio* is of course a regular commercial article, as are also certain others which can be obtained correctly labelled, such, for example, as the oil of *Pinus sibirica*. In addition to the difficulties arising from this confusion in the names, gross adulteration with turpentine is regularly met with. The ester to which the oil owes the character of its odour, bornyl acetate, can be obtained on the market, but it has not ousted the natural oils from the position they hold both as perfumes and drugs. For certain throat affections they find regular employment either as inhalations or for internal administration.

Cypress-leaf Oil.—The leaves of *Cupressus sempervirens* yield about 1 per cent. of an oil of specific gravity about 0·890, and optical rotation + 4° to + 16°, consisting largely of terpenes. It is soluble in 4 to 5 volumes of 90 per cent.

Table of Fir and Pine Needle Oils, etc.

Oil.	Sp. Gr.	Rotation.	Constituents.
Abies excelsa (leaves)	·865-·888	− 20° to − 40°	Pinene, limonene, cadinene, bornyl acetate (5 to 10 per cent.).
„ „ (young cones) . . .	·855-·870	− 60° to − 80°	Pinene, limonene, bornyl acetate (·5 to 1 per cent.).
Pinus sylvestris (German and Swedish) .	·872-·885	+ 7° to + 13°	Pinene, sylvestrene, dipentene, cadinene and bornyl acetate (3·5 per cent.).
„ „ (English) . . .	·885-·890	− 7° to − 20°	Bornyl acetate (3 per cent.).
„ pumilio	·859-·875	− 3° to − 10°	Pinene, phellandrene, sylvestrene, cadinene, bornyl acetate (4 to 7 per cent.).
Larix decidua	·878	+ 0° 22′	Bornyl acetate (6·5 per cent. ; borneol, 6 per cent.).
Abies sibirica	·910-·920	− 30° to − 45°	Bornyl acetate.
Picea vulgaris	·888	− 21° 40′	Pinene, phellandrene, dipentene, cadinene, bornyl acetate.
Pinus nigra	·925	− 39° 40′	Bornyl acetate (50 per cent.).
„ montana	·865-·875	− 4° to − 9°	Bornyl acetate (5 to 7 per cent.).
„ palustris	·861	+ 23° 55′	
„ strobus	·901	− 40°	Bornyl acetate (9 per cent.).
„ cubensis	·868	+ 9° 6′	
„ cembra	·880	+ 29°	
Abies balsamea	·892	− 29° 1′	Pinene (?), bornyl acetate.
„ canadensis	·907-·913	− 18° to − 26°	Pinene, camphene, cadinene, bornyl acetate (50 per cent.).
Picea nigra	·913	− 23° 50′	Bornyl acetate (38 per cent.).

alcohol. It is a somewhat expensive oil, said to be very useful as a remedy for whooping cough when inhaled.

Schimmel & Co. have recently examined this oil. It had a specific gravity 0·892, optical rotation + 16° 5′, and refractive index 1·4742. Its saponification number was 25·3, and its acetyl-saponification number 50·5. It was not soluble in 10 volumes of 90 per cent. alcohol. It was found to contain traces of furfurol, dextro-pinene, dextro-camphene, dextro-sylvestrene, cymene, a ketone yielding a semicarbazone melting at 177°, a second ketone not yet characterised, sabinol (?), a terpene alcohol (possibly geraniol), and the acetic and valeric esters of dextro-terpineol. The terpenes make up 65 per cent. of the oil, the principal portion consisting of camphene and sylvestrene.

OILS OF THE ANGIOSPERMS.—I. MONOCOTYLEDONS.

N. O. Gramineæ.

The essential oils of this natural order are obtained principally from the family formerly known as *Andropogon*.

1. Palmarosa oil from *Andropogon Martini*.
2. Ginger-grass oil, described as inferior palmarosa, or a mixture of the latter with turpentine or mineral oil, but probably when pure derived from a species not definitely identified.
3. Lemon-grass oil from *Andropogon citratus*, DC.
4. Vetiver oil from *Andropogon muricatus*, Retz.
5. Citronella oil from *Andropogon nardus*, L.
6. Oil of *Andropogon odoratus*, Lisb.
7. Camel-grass oil from *Andropogon laniger*, Desf.

Several of these are commercial products of the highest importance, as they are used on an enormous scale either for direct perfumery, or for the preparation of perfumes of an entirely different nature, by chemical methods. For many

years the exact botanical sources of these oils has been a matter of doubt, and many misleading names have been used, but, in the case of the more important oils, at all events, these may now be regarded as settled.

The confusion, however, has now been cleared up, and Stapf (*Kew Bulletin*, 1906, 8, 297) has dealt in a masterly manner with the subject. He considers that the subgenera *Cymbopogon* and *Vetiveria* are sufficiently distinct to be recognised as genera, and he has therefore introduced the necessary change in nomenclature. In this manner the plants referred to become renamed as follows :—

Old Name.	*New Name.*
Andropogon Martini	Cymbopogon Martini.
,, nardus	,, nardus.
,, citratus	,, citratus.
,, muricatus	Vetiveria zizaniodes.
,, odoratus	(Remains as before).

Citronella Oil.—This oil is distilled from the "Indian grass," *Andropogon nardus* (*Cymbopogon nardus*), chiefly in Ceylon. It is a pale yellow oil of very powerful odour, on which account, together with its low price (varying on the market from about 1s. to 2s. per lb. lately), it is more extensively employed in cheap soap perfumery than any other essential oil. The chemistry of the oil was first seriously attacked by Dodge (*American Journal of Chemistry*, xi., p. 456), who showed that it contained a large quantity of the aldehyde citronellal. Other workers have since shown that it contains, in addition, the terpenes camphene, laevo-limonene and dipentene, the alcohols geraniol and linalol and small quantities of borneol and methyl-heptenone. Traces of methyl-eugenol and of two sesquiterpenes also exist.

The oil found on the market is frequently adulterated with certain varieties of kerosene, and probably with resin spirit, and occasionally with an oil whose identity is not yet

settled, but which appears to be somewhat similar in properties to the oil of gurjun balsam.

It is now well recognised that the commercial citronella oil arriving here in drums is never pure. It is sold on a guarantee to pass "Schimmel's test," which was at one time interpreted very strictly as meaning that the oil should be soluble in 2 to 3 volumes of 80 per cent. alcohol, and that, by the addition of more alcohol up to 10 volumes, nothing more than opalescence should result. The test now adopted by the London market, however, is as follows: 1 volume of the oil when shaken with 10 volumes of 80 per cent. alcohol should yield a solution, which shall not be more than faintly turbid, and from which no oil globules, visible to the naked eye, shall separate after standing for twenty-four hours. Schimmel's so-called "raised test" excludes more than a small amount of adulteration and consists in first adding to the oil 5 per cent. of its volume of kerosene, when the oil should then pass the ordinary "Schimmel's test".

M. K. Bamber (*Proc. Chemical Society*, 1903, 292), the Government analyst of Ceylon, gives a new method which he claims will rapidly determine the percentage of adulterant in citronella oil.

A mixture of 2 c.c. of pure, acid free coconut oil and 2 c.c. of the citronella oil to be examined is shaken for one minute with 20 c.c. of 83 per cent. alcohol (specific gravity 0·8273 at 30°) in a graduated tube, which is then rotated in a centrifugal machine for a minute. The volume of coconut oil which now contains the impurity originally present in the citronella oil is read off, and the amount minus the 2 c.c. represents the adulterant. The author has examined this process and finds that it is useless, and cannot understand how it could ever be suggested seriously as a scientific analytical process. It involves, *inter alia*, the assumption that all adulterants of citronella oil are of such a character in regard to their solu-

bility that coconut oil can completely extract them from a solution in a mixture of citronella oil and 83 per cent. alcohol. It is possible that one might approximately estimate the amount of coconut oil present in this way, but certainly not adulterants as a general rule.

The specific gravity of the pure oil is very variable, and while it is not possible to define the limits closely, it may be taken that anything outside ·885 to ·920 is impure. The optical rotation, which is laevo-rotary, varies with the specific gravity, the oils with a high gravity being more highly rotary than those with a lower gravity. The refractive index of Ceylon oil is usually about 1·4800 and that of Java oil 1·4660. Other criteria of the purity of the oil are its solubility in alcohol and its acetyl number. One volume of a really pure oil should yield a clear, or at most, slightly opalescent solution with 2 to 3 volumes of 80 per cent. alcohol at 20°, and no oily drops should separate even when 10 volumes of the alcohol are added. It is important in the case of pure oils that the clearness of the solution of the oil in 3 volumes of the alcohol should not be impaired by the addition of more alcohol, as although kerosene will render it partially insoluble in the smaller quantity of alcohol, an adulterant has been noticed which only rendered the solution turbid when more of the 80 per cent. alcohol was added. The nature of this has not been determined (*vide supra*).

The acetylation method is of considerable value. Although sometimes spoken of as the estimation of geraniol, this is incorrect; for citronellal is easily converted into isopulegol acetate by acetic anhydride, with the result that, although the determination may be calculated as geraniol, it actually includes the citronellal as well. A useful and comparative result is thus obtained. This is emphasised by the following figures quoted by Schimmel & Co. for fourteen samples, which they are convinced were pure (*Report*, Oct., 1898).

	Rotation.	*Sp. Gravity.*	*Geraniol.* Per cent.
1	−0° 46′	·892	88·6
2	−0° 54′	·892	80·9
3	−0° 48′	·892	82·5
4	−1° 18′	·890	85·4
5	−1° 32′	·886	85·1
6	−2° 20′	·888	83·4
7	−1° 25′	·894	81·8
8	−0° 53′	·890	90·6
9	−7° 10′	·919	56·9
10	−0° 34′	·888	86·4
11	−9° 53′	·915	65·5
12	−20° 37′	·896	50·4
13	−7° 13′	·918	54·1
14	−9° 36′	·908	61·1

The author and C. T. Bennett have carried out a number of experiments on pure citronella oil and have proposed as standards for pure Ceylon oil (*i.e.*, the Lena Batu oil) the following figures. It may be noted that the presence of any quantity of resin spirit or of kerosene will usually cause the specific gravity of the first 10 per cent. distilled to be distinctly lower than 0·858:—

Specific gravity	0·900 – 0·915
Rotation	0° to − 15°
Sp. gr. of 1st 10 °/₀ (distilled at 20-40 mm.)	above 0·858
Refractive index of same at 20°	above 1·4570
Solubility in 80 °/₀ alcohol	to pass Schimmel's test.
Geraniol and citronellal (calculated as total geraniol)	above 58 °/₀

Umney and Swinton (*Year Book of Pharmacy*, 1897, p. 365) have endeavoured to explain the differences in the commercial oils of apparently genuine character. They then came to the conclusion, chiefly by means of experimental distillation of the oils with steam, that the high gravity oils are the native distilled oils over an open fire, whilst the lower gravity oils are steam distilled, and that the differences do not at all depend on any variation in the grass used. The high specific gravity is regarded as being due to a hitherto

undescribed sesquiterpene, and the high optical rotation to a highly active terpene.

It is, however, now well established that there are two different kinds of citronella grass distilled in Ceylon, but whether they are true varieties, or whether one is merely a degeneration, is not yet known. Under any circumstances, it is certain that the high gravity oils are of poorer odour, containing much less aldehyde and alcohol, to which the oil chiefly owes its value. The grass yielding the oil with high geraniol content is known as Maha Pengiri, and that yielding the oil with low geraniol content as Lena Batu.

A pure Lena Batu oil contains about 30 per cent. of citronellal and 30 per cent. of geraniol; whilst a Maha Pengiri oil contains up to 50 per cent. of citronellal and 38 per cent. of geraniol.

The aldehyde citronellal, possessing the characteristic odour of the oil, is also a commercial product. It is, however, from fifteen to twenty times as expensive as the oil itself, and certainly does not possess any commensurate advantages. The purest commercial samples examined by the author were slightly optically active, perfectly colourless liquids, of specific gravity about ·873.

The grass is cultivated almost entirely in the south of Ceylon. According to Fritzsche, somewhere between 40,000 and 50,000 acres are devoted to it, and but little attention is necessary. The growth is continuous, and three harvests can be obtained annually in very favourable years, but usually two are found sufficient—one in July or August and one in December, January or February. The yield of oil is about sixteen to twenty bottles (22 oz.) per acre for the summer crop, and five to ten for the winter crop. After a lapse of fifteen years the plants become exhausted, and new plants become necessary. There are somewhere about 600 stills at work on the island, and the enormous output of well

over 1,000,000 lb. per annum shows to what an extent this oil is used. So powerful is its odour and so cheap is the oil that it is now frequently used not only for perfuming cheap toilet soap, but also to cover the disagreeable odour of common hard and soft soap. The distilleries are usually in a shed, and consist of a steam boiler with a safety valve and water indicator, resting upon a solid foundation, two cylindrical stills about 6 ft. to 7 ft. high, and 3 ft. to 4 ft. broad. These are connected with a spiral condenser in a tub of cold water, the oil eventually being collected in a receptacle underground, which can be locked in order to prevent the natives from stealing it. The accompanying diagram, reproduced from the *Chemist and Druggist*, illustrates the arrangement (p. 176).

The oils distilled in Java and the Straits Settlements resemble that from the grass known as Mahi Pengiri in all particulars. The following figures are those for typical oils of this class, as compared with Ceylon commercial Lena Batu oil:—

	Perak.	*Ceylon.*	*Java.*
Specific gravity . . .	0·8948	0·892	0·908
Optical rotation . . .	−1° 34′	−2° 25′	−9° 35′
Refractive index . . .	1·4858	—	—
Solubility in 80 % alcohol .	1 in 1	1 in 1	1 in 1
Geraniol	32·7 %	38·9—38·1 %	32·9 %
Citronellal	55·3 %	50·4—55·3 %	28·2 %

The following tables by the author and Bennett show the whole aspect of the Ceylon citronella oil question.

The physical characters of the chief constituents of citronella oil which affect the question are as follows:—

	Sp. Gr.	*Rotation.*	*Refractive Index.*
Camphene . . .	0·864	− 62°	1·4637
Dipentene . . .	0·847	− 54°	1·4691
Citronellal . . .	0·854	+ 12°	1·4481
Sesquiterpene . . .	0·864	+ 1° 30′	1·5185
Geraniol	0·883	± 0°	1·4739 at 23°

The following figures are the results of examinations of pure and adulterated samples :—

TABLE I.—PURE CITRONELLA OILS.

Characters of first 10 per cent. distilled at 20 to 40 mm. pressure.

	Sp. Gr. at 15·5°.	*Rotation in* 100 *mm. Tube.*	*Refractive Index at* 19° *C.*
A . . .	0·861	– 44°	1·4680
B . . .	0·861	– 43°	1·4732
C . . .	0·860	– 35°	1·4692
D . . .	0·863	– 23°	1·4655
E[1] . . .	0·866	– 6°	1·4590
F[2] . . .	0·867	– 11°	1·4571

TABLE II.—CITRONELLA OILS MIXED WITH ADULTERANT.

Characters of first 10 per cent. distilled at 20 to 40 mm. pressure.

	Sp. Gr. at 15·5°.	*Rotation in* 100 *mm. Tube.*	*Refractive Index at* 19° *C.*
1 E + 5 p.c. resin spirit	0·855	– 7°	1·4563
2 E + 10 p.c. ,,	0·848	– 3°	1·4545
3 E + 15 p.c. ,,	0·841	– 2°	1·4525
4 E + 20 p.c. ,,	0·833	– 1°	1·4505
5 D + 5 p.c. ,,	0·854	– 17°	1·4570
6 D + 10 p.c. ,,	0·845	– 14°	1·4515
7 D + 20 p.c. ,,	0·835	– 8°	1·4490
8 C + 10 p.c. petroleum spirit	0·848	– 24°	1·4514

TABLE III.—ADULTERATED CITRONELLA OILS ON THE MARKET.

Characters of first 10 per cent. distilled at 20 to 40 mm. pressure.

	Sp. Gr. at 15·5°.	*Rotation in* 100 *mm. Tube.*	*Refractive Index at* 19° *C.*
1	0·822	– 26° 48′	1·4492
2	0·824	– 23° 50′	1·4504
3	0·833	– 18° 20′	1·4525
4	0·820	– 22°	1·4486
5	0·844	– 17° 30′	1·4540
6	0·836	– 29°	1·4495

[1] E is an oil from the Straits Settlements.

[2] F is a Ceylon oil distilled by Winter, and probably prepared by fractionation.

TABLE IV.—RESIN AND PETROLEUM SPIRITS.

Characters of first 10 per cent. distilled at 20 to 40 mm. pressure.

	Sp. Gr. at 15·5°.	*Rotation in* 100 *mm. Tube.*	*Refractive Index at* 19° *C.*
1 Resin spirit . . .	0·806	+ 4°	1·4403
2 Resin spirit . . .	0·802	+ 2° 30′	1·4425
3 Petroleum spirit[1] (turpentine substitute) .	0·798	+ 1°	1·4435
4 Petroleum spirit[1] (turpentine substitute) .	0·801	+ 1° 30′	1·4416

The lightest fraction which the author and Bennett obtained from the adulterated oils had a specific gravity of 0·798, an optical rotation of − 17°, and commenced to distil at 112° C. In none of the fractions has any odour of paraffin been observed, nor any fluorescence—hence the conclusion that resin spirit is the adulterant.

Suggested Standard.—From a consideration of these figures the following standards for pure citronella oil are suggested:—

1. The oil must dissolve either clear, or at most with the slightest opalescence, in 10 volumes of 80 per cent. alcohol at 20° C.

2. The first 10 per cent. distilled under reduced pressure (20 to 40 mm.) must have a specific gravity not below 0·858 and a refractive index at 20° not below 1·4570.

It may be regarded as fairly certain that no adulterated sample will pass these tests, although the limit for refractive index has been placed lower than the figures found for normal Ceylon oils, in order to meet the requirements of other oils, such as those from Java or the Straits Settlements, and, in general, those with low terpene-content. But any adulterated

[1] The actual source of these turpentine substitutes has not been ascertained, as the distillers decline to give information. They have a faint odour of paraffin, and a distinct though slight fluorescence, and probably consist only in part of petroleum spirit.

oil which might show a higher refractive index than has been indicated would fail to pass the specific gravity limit if anything more than traces of adulterant were present.

A still 7 ft. high and 4½ ft. in diameter produces about 350 to 450 oz. per day. Most of them are as that illustrated, although there are some which are arranged for an open-fire distillation.

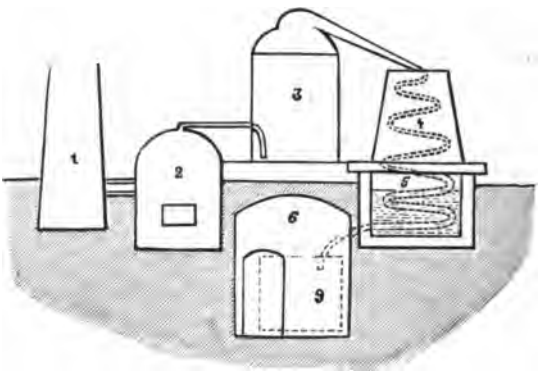


FIG. 14.—Citronella Oil Still.
1, chimney; 2, steam boiler; 3, still; 4 and 5, condenser; 6, underground cellar; 9, receiver.

Lemon-grass Oil.—This oil is the product of distillation of the grass *Cymbopogon citratus* and *Cymbopogon flexuosus*. Ceylon and Straits Settlements oil are derived from the former, and Malabar and Cochin oil from the latter. Cochin China, Ceylon and Singapore were the chief centres of cultivation, although the grass is found over a very wide tract of the Indian peninsula and in the West Indies, which now produce a considerable amount of the oil. The greater part is exported from the ports on the Malabar coast. With regard to its preparation, much that has been mentioned under citronella oil holds good here also, but, of course, the fact that the oil does not enjoy nearly so large a consumption as

citronella oil accounts for its preparation being more in the hands of the natives than the last-named oil. The annual production of lemon-grass oil appears to be about 50,000 lb. Its chief use is for perfumery, in which it plays an important part, as it has an odour resembling the true verbena, and is often known as Indian verbena. A large amount is consumed in the manufacture of ionone. With regard to price, it has been the subject of speculative dealings, hence it has varied from a few pence—1½d. even at one time—to about 1s. an ounce during the last few years. In addition to its extensive use in perfumery, it has lately found considerable employment for the preparation of citral, its chief constituent, for the manufacture of ionone. It is also used to some extent either as it is, or as citral, to adulterate oil of lemons. Attempts have been made, successful to an extent, but utterly misleading in their effects, to make the citral content the basis of the value of oil of lemons. Hence the addition of small quantities of lemon-grass oil or citral to lemon oil. This will be again referred to under that oil.

The East Indian variety of lemon-grass oil is a yellow to brownish oil, of specific gravity ·895 to ·905. It is often practically inactive optically, and should never vary more than from + 3° to − 3°. Its refractive index is about 1·4880. It is often adulterated with fixed oils, which not only alter its specific gravity, but also interfere with its solubility in alcohol. When pure, it dissolves to a clear solution in three times its volume of 70 per cent. alcohol and does not usually become turbid by further additions of alcohol. Its most important constituent is citral, which occurs in it to the extent of from 70 to 85 per cent. In addition to this, methyl-heptenone and geraniol, traces of citronellol, and possibly linalol, have been found. Terpenes occur to the extent of about 10 per cent. According to Stiehl, these consist of limonene and dipentene, and there is also a trace of cymene.

These are the only constituents which can be said to be known to exist in the oil.

West Indian lemon-grass oil differs in its character from the East Indian oil. It is much less soluble than the other variety, and is usually rectified in the West Indies in order to increase its solubility. The author is informed that when so rectified it dissolves in 3 volumes of 70 per cent. alcohol, but after keeping a short time it becomes insoluble again. It certainly always arrives in London in this state, and will not dissolve to a quite clear solution in 10 volumes of 70 per cent. alcohol. This is probably due to the presence of an easily oxidisable olefenic terpene which the author is now investigating. West Indian lemon-grass oil has the following characters:—

Specific gravity	0·877-0·887
Optical rotation	+ 2° to − 2°
Total aldehydes	76 % to 85 %
Refractive index	1·4875

It is not clearly soluble in 70 % alcohol.

A Mexican lemon-grass oil examined by Schimmel & Co. had a specific gravity 0·885, optical rotation 0°, and citral 70 per cent. Under the name "Java lemon oil" several samples have been reported on by the same firm, and found to contain 50 per cent. of citral; this oil is probably the distillate of some other *Andropogon* species.

The author has once observed the use of acetone as an adulterant of lemon-grass oil. This is shown by the diminution in volume on shaking the oil with water, and can be separated by distillation, the acetone coming over at a very low temperature. The oil is chiefly dependent, if not entirely so, for its value on the percentage of citral it contains. Hence it is of importance to be able to estimate this constituent, at all events, with some degree of accuracy. This can be done by shaking the oil with solution of bisulphite of sodium, as

described in a former chapter. It must be remembered, however, that this is only an approximate estimation, as a certain amount of the citral is converted into water soluble sulphonic acid derivatives, and a certain amount remains unabsorbed. For comparative purposes, however, it is exceedingly useful. The preparation of ionone (artificial violet) from lemon-grass oil direct, and from the separated constituent, citral, is the subject of numerous patents. From this point of view it is important to know if citral is really the main constituent of the oil. If it were not so, the correctness of the patent specifications would be open to attack, and the results might be of importance. According to most chemists who have worked seriously on this oil, citral is the only aldehyde present in the oil, with the exception of traces of an isomeric aldehyde, and of citronellal. Upon this point Tiemann, Semmler and Doebner, the three chief authorities on this oil, are completely agreed. Stiehl (*Jour. prakt. Chem.*, 1898, p. 51) has claimed to have separated the aldehydic constituent into three different bodies. He urges that the large amount of citral found in the oil usually, is due to the isomerisation of the other aldehydes by means of the bisulphite of sodium used in separating it, which is generally too acid. If this salt be perfectly pure he claims that this isomerisation does not take place. These aldehydes he terms citral (the aldehyde usually known as such), allolemonal and citriodoraldehyde, and he gives the following as their properties:—

	Citriodoraldehyde.	*Allolemonal.*	*Citral.*
Boiling point	228°-229°	233°-235°	225°-227°
Sp. gravity at 20°	·8883	·9017	·8868
Rotation	0°	− 5° 6′	0°
Melting point of compound with naphthocinchoninic acid . .	204°	235°	197°

Doebner, however, has shown—in the author's opinion conclusively—that these other aldehydes are merely impure

citral, and that the former statements made regarding the oil are correct. Tiemann and Semmler have also repeated their former work and confirmed it in every respect (*see also under* "Citral"). It must be remembered that by the body citral it is intended to denote the mixture of stereoisomers *a*-citral and *β*-citral. Lemon-grass oil is also known locally as Sereh oil and by the Tamils as Vāsana-pillu ("perfume grass") or Karpūra-pillu ("camphor grass").

It will be convenient to here refer to an oil which contains much citral. The oil is derived from the leaves of a small tree (*Backhousia citriodora*, N. O. *Myrtaceæ*) indigenous to Southern Queensland. It is very similar in composition to lemon-grass oil, from which it can scarcely be distinguished by smell. It contains, however, a larger percentage of citral, and should prove a remunerative source of citral for the preparation of artificial violet essence. Gildemeister and Hoffmann examined this oil, and have stated that it consists almost entirely of citral.

Samples have been examined by Umney. The oil has the following characters:—

Specific gravity . .	0·895-0·896
Optical rotation . .	Inactive or only slightly laevo-rotatory
Refractive index . .	1·4889
Aldehydes (principally citral)	94·95 % by absorption with $NaH.SO_3$.

It is soluble in 2½ to 3 volumes of 70 per cent. alcohol, and distils almost entirely between 215° and 230° C. It is practically free from terpenes, but appears to contain traces of other bodies which give it a characteristic odour of its own, in addition to the strong citral odour. The first 10 per cent. distilled had a penetrating odour resembling an amyl ester. The characters of the first and last fractions are appended:—

	First 10 %	Last 5 %	Residue 5 %
Specific gravity	0·886	0·895	—
Rotation	Nil	Nil	—
Refractive index	1·4798	1·4907	1·5132

The high refractive index of the residue indicates the presence of traces of sesquiterpene. This oil must not be confounded with that of *Eucalyptus citriodora* (a tree also indigenous to Queensland), which consists almost entirely of citronellal.

Indian Geranium Oil.—This oil is in no way related to true geranium oil, except on account of its similar odour. It occurs in European commerce under the names "Indian geranium oil," "Turkish geranium oil" and "palmarosa oil". Distinctions have often been made between these commercial products, but it appears certain that the only differences existing between them are those of fineness of odour and freedom from adulteration. The oil is distilled in India from the grass *Cymbopogon Martini*, formerly known as *Andropogon Martini*, or *Andropogon Schœnanthus* by some botanists, but it must be understood that the *Andropogon Schœnanthus* of Linnæus is an entirely different grass, which grows wild in large tracts in the northern and eastern provinces, especially in the North-West and the Punjaub; it is also abundant in the Deccan, Central India and Kashmir. According to Schimmel, the most productive districts are Nagpore-Khandesh and Jubbulpore. The following account, from part vi. of *Pharmacographia Indica*, is particularly interesting: "The oil distillers in Khandesh call the grass *Motiya* when the inflorescence is young and of a bluish-white colour; after it has ripened and become red, it is called *Sonfiya*. The oil obtained from it in the first condition has a more delicate odour than that obtained

from the ripened grass. The *Motiya* oil is usually mixed with the second kind, which by itself would not fetch a good price in the European market. The grass grows freely, though not very widely, on open hillsides in West Khandesh, especially in Akráni. The original seat of the manufacture was Pimpalner, but as the oil is in great demand, the manufacture has of late spread to Nandurbár, Sháháda and Taloda. The makers are Mussulmans, who at the close of the rains, about September, when the grass is ripening, buy it from the Bhils, stack it and set stills at the sides of brooks where wood and water are plentiful. In 1879-1880 the number of stills was 197, producing about 71 cwt. of oil. More than 100 stills are worked in Nandurbár alone, and the increase of the manufacture is prevented only by the scarcity of the grass. The yield is about ·3 per cent. The oil is packed in skins and sent on bullock back over the Kundaibári Pass to Surat and by Dhulia and Manmad to Bombay." From Bombay it is exported to the Red Sea ports, Constantinople, Trieste and London. The oil is a pale yellow liquid (often dark on account of the crude methods of distillation used by the natives, wherein too little water is used in the stills, with the result that the grass is burned), but sometimes water white when rectified. It has a characteristic geranium odour, and is a most popular perfume where an odour recalling roses and geranium is required at a comparatively low price. When pure the oil has a specific gravity of from ·885 to ·896 and is almost inactive optically, rotating from − 2° to + 2°, usually under 1° either way, and rarely up to + 4°. The oil should dissolve in three times its volume of 70 per cent. alcohol. Its refractive index is about 1·4800. The ascertained constituents of the oil are the alcohol geraniol, esters of this alcohol (chiefly the acetic and caproic esters), methylheptenone and the terpene dipentene. The odour

value is entirely due to the geraniol and its esters, hence their estimation becomes of some importance. The esters do not require less than 3 nor more than 5 per cent. of potash for saponification. The usual amount of esters present is from 10 to 15 per cent. The free geraniol varies from 65 to 85 per cent. This is estimated in the usual way by acetylation —converting the geraniol into its acetic ester, and saponifying, as described in a previous chapter. The total geraniol (free and combined) varies from 78 to 92 per cent.

Schimmel & Co. give the following figures for four pure samples :—

GERANIOL.

	Combined.	*Free.*	*Total.*
1	12·1	76·36	88·46
2	13·55	69·98	83·33
3	8·67	68·23	76·9
4	8·48	83·15	91·63

The oil is often adulterated, notably with fixed oils and with turpentine or petroleum oil, sometimes with citronella and ginger-grass oils. Turpentine and petroleum are easily detected, as they greatly interfere with the solubility in alcohol, and, in the case of fatty oils, the sample will leave a non-volatile residue when steam distilled. When turpentine is added, the optical activity may be altered and the ester and geraniol contents lowered.

The legitimate use of this oil is, of course, for perfumery, in which rôle it is handicapped by the finer odour of the true geranium oils. The difference in price, however, acts largely as a set-off in this respect. The active body geraniol is also a commercial product now, being prepared from various sources, notably from citronella oil. The rhodinol of commerce appears to be a mixture of geraniol and other alcohols, chiefly citronellol. Both of these bodies are, however, more expensive than the Indian geranium oil.

It also finds extensive use as an adulterant of either otto of roses, or of true geranium oil, the latter being also sometimes employed to adulterate otto of roses. An extraordinary use for this oil is suggested by Balfour in the *Cyclopædia of India*. He says that "grass oil has the property of preventing the loss of hair that occurs after some acute diseases: it is said to produce a new growth of hair". Whether this is true or not is uncertain. Locally, this oil is known as Rusá oil.

Oil of Ginger-grass.—This oil has long been regarded as an inferior or adulterated palmarosa oil, but its individuality is now clearly established, although its botanical source is still not known.

Pure ginger-grass oil has a specific gravity of about 0·935 to 0·942, and an optical rotation of + 19° to + 25°. The oil is soluble in 3 volumes of 70 per cent. alcohol, and contains but little ester, but a high amount of free alcohols, up to over 90 per cent. in good samples. These figures may require some revision, as not a great many authentic samples have been examined. Schimmel & Co. have investigated the oil and find present phellandrene in small quantity. They find that the alcohols present consist of a mixture of geraniol with di-hydrocumic alcohol $C_{10}H_{16}O$. The pure di-hydrocumic alcohol had the following characters: boiling point at 767 mm. = 227°; specific gravity = 0·951 $[\alpha]_d = -13° 18'$; refractive index, 1·4963. It forms a well-defined naphthylurethane melting at 146° to 147°. Traces of a solid fatty acid are present in the form of esters. Traces of inactive carvone are also present in this oil as well as dextro-limonene, dipentene, and an aldehyde $C_{10}H_{16}O$, boiling at 76° to 78° at 5 mm., or at 221° to 224° at 754 mm., and having a specific gravity 0·935 and refractive index 1·4735. It is optically inactive.

Oil of Veti-vert.—This oil, also known as oil of vetiver or oil of cuscus, is the product of distillation of the root of

Vetiveria zizanoides, formerly known as *Andropogon muricatus*, Retz. These roots are known in Bengal under the name of khas-khas, from which the name cuscus is easily traced. The plant is a perennial tufted grass growing to a good height, and is found all over the country near the Coromandel coast, Mysore, Bengal, Burma and the Punjaub. It is also found in Réunion and Mauritius and in the West Indies. In contradistinction to the grasses above described, the leaves themselves are practically odourless, whilst the roots have a strong, agreeable odour. On distillation, the first fractions passing over are much more volatile and lighter than those which come over with difficulty towards the end of the distillation. These "light" and "heavy" oils can be separated by using a steam-jacketed still with steam at a pressure of about 10 lb., until no more oil comes over. The heavy oil is then obtained by passing steam at a higher pressure direct into the retort. The oil distilled in Europe, however, is usually, if not always, a single distillate, and the fractionated oils are scarcely commercial articles. Réunion distilled oil is, however, of much lighter specific gravity than European distillates, and is usually found to vary from 0·980 to 0·995. The yield of oil is a matter of much disagreement. According to Piesse, 100 lb. of oil yield about 9 or 10 oz. of oil, whilst Watts states that only 2 oz. are obtained. Other observers give from ·4 to ·9 per cent. Probably about 1 per cent. is the usual average. Much of the oil (which is entirely used for high-class perfumery) as found in commerce is adulterated, frequently with a fixed fatty oil. But little is known of the chemistry of its constituents, and only a comparatively few samples have been examined at all. The specific gravity of the unfractionated oil, *i.e.*, as it is distilled from the root, is 1·01 to 1·03. It is dextro-rotary, + 25° to + 40°, and should give a clear solution with 1½ to 2 volumes of 80 per cent. alcohol. The ester value lies between

60 and 80. Schimmel & Co. give the following figures for perfectly genuine samples of their own distillation :—

Specific gravity	1·019 to 1·027
Optical rotation	+25° to + 26°
Ester number (as per cent. KOH) .	7 to 8
Solubility in 80 per cent. alcohol .	1 in 1½ to 2.

A sample was fractionated with the following results :—

B.P. at 23 mm.	Per cent.	Rotation.
144°-164°	8	− 4° 10′
164°-170°	10	− 3° 20′
170°-180°	24	+ 2° 5′
180°-185°	30	+ 31° 40′
185°-200°	20	+ 47° 5′

From the point of view of the practical perfumer, this oil (which is somewhat expensive when pure) is said to blend excellently with the odours of orris root and "cassie" flowers (*Acacia Farnesiana*).

In the distillation of this oil traces of methyl alcohol, furfurol and diacetyl are found in the distillation waters. Genvresse and Langlois have isolated a sesquiterpene from the oil, $C_{15}H_{24}$, which they term vetivene. It boils at 262° to 263° at 740 mm., and has a specific gravity 0·932 and optical rotation + 18° 19′. A sesquiterpene alcohol, $C_{15}H_{26}O$, was also isolated, which the discoverers term vetivenol. It boils at 169° to 170° at 15 mm., and has a specific gravity 1·011 at 20° and optical rotation + 53° 43′.

The above-described are the Indian grass oils of which we possess reliable knowledge. The only ones in addition which need be here mentioned are the so-called "camel grass" oil, obtained by distilling the grass formerly known as *Andro-*

pogon laniger (but now recognised as the *Andropogon Schœnanthus* of Linnæus, and renamed *Cymbopogon Schœnanthus*), and the oil from *Andropogon odoratus*. The camel grass grows freely on the lower Himalayas and in Thibet, and has been found in Beluchistan. Dr. Dymock distilled some of the fresh plant, and states that the yield was 1 per cent. According to Schimmel, the oil has an odour of elemi, a specific gravity 0·905 to 0·919, and is optically active from $-4°$ to $+34° 38'$. It contains phellandrene, and boils between 170° and 250°.

The oil from *Andropogon odoratus*, which is obtained by distillation from the grass, has a specific gravity 0·915 to 0·935, and is laevo-rotary $-22°$ to $-23°$. The yield is under ·5 per cent.

N. O. Aroideæ.

Calamus Oil.—This oil is distilled from the rhizome of the sweet flag, *Acorus calamus*. This plant is a member of a family with aquatic tendencies, and is probably a native of Asia, although now found largely in Europe. Although the essential oil obtained from the rhizome is known either as *Ol. Acori calami* or *Ol. Calami aromatici*, the plant must not, as Pereira points out, be confused with the *Calamus aromaticus* described by Royle, which is one of the *Andropogon* family. The banks of European rivers afford a plentiful supply for the markets, and it is also cultivated in damp swamps in India. The fragrance of the plant and its oil appears to increase as the climate in which it is cultivated is warmer. Commercial rhizome of European origin is obtainable in the shops, and occurs as somewhat flattened pieces of about 4 inches long and about $\frac{3}{4}$ of an inch thick. Keeping does not improve it, nor does the process of decorticating it, as is often done for appearance sake. Many of the essential oil glands occur in the outer layers of the rhizome, so

that the process of peeling naturally lessens the odour value. Dymock thus describes the Indian rhizome in his *Notes on Indian Drugs*: "The root stock occurs in somewhat tortuous, sub-cylindrical or flattened pieces, a few inches long and from ½ to 1 inch in greatest diameter. Each piece is obscurely marked on the upper surface with the scars, often hairy, of leaves, and on the under with a zig-zag line of little, elevated dot-like rings, the scars of roots. The root stock is usually rough and shrunken, varying in colour from dark brown to orange brown, breaking easily with a short, corky fracture, and exhibiting a pale brown spongy interior. The odour is aromatic and agreeable, the taste bitterish and pungent." The powdered rhizome is used for sachet and toilet powder. From dried German rhizome, Schimmel obtained about ·8 per cent. of essential oil, whilst the fresh root yields from 1·5 to 3·5 per cent. Japanese root yields as much as 5 per cent. The oils do not quite agree in their chemical properties, and that from the green rhizome has a finer odour than that from the dried. The chief difference noticeable is that the oil from green root is more soluble in weak alcohol than that from the dried. But little is known of the chemistry of this oil. Kurbatow states that there is a large proportion of a terpene boiling at 158° to 159° present, which forms a crystalline hydrochloride melting at 65°. Its specific gravity was ·8793 at 0°. From the author's knowledge of this oil, this terpene was probably impure pinene. In addition to this there appear to exist a sesquiterpene and certain oxygenated constituents not yet identified; by distilling off the terpenes under reduced pressure, the residual oil has a specific gravity of from 1·000 to 1·018, which indicates the high specific gravity of the oxygenated constituents of the oil. Von Soden and Rojahn have also isolated a crystalline compound of the formula $C_{15}H_{26}O_2$ melting at 166° from Galician calamus oil.

Schimmel & Co. give the following figures for eleven samples distilled by themselves:—

Specific Gravity.	*Optical Rotation.*
·970	+ 20° 44′
·962	+ 31°
·969	+ 18°
·967	+ 20°
·963	+ 15° 50′
·964	+ 16° 47′
·967	+ 17° 10′
·966	+ 27° 12′
·966	+ 13° 8′
·966	+ 22° 55′
·969	+ 15° 10′

These figures are almost sufficient to place the limits of, say, ·960 to ·970 for gravity and + 10° to + 35° for optical rotation, except in the case of Galician oils, which are often of lower rotation. Oil from Japanese root, however, does not agree with these, as its specific gravity rises to 1·000, indicating its comparative freedom from terpenes. As a further test, all pure samples are soluble in all proportions in 90 per cent. alcohol. This oil is used extensively for the preparation of aromatic cordials, beers and liqueurs, and also for perfuming toilet articles and snuffs. An oil is also distilled from the fresh leaves of the plant. The yield is from ·2 to ·3 per cent. of an oil of specific gravity ·965 and optical rotation about + 20°.

It is possible that the Japanese oil is derived from the rhizome of *Acorus spuriosus*. At all events, it is obtained to the extent of 5 per cent. from the rhizome, and has a specific gravity 0·992 or above and boils between 210° to 290°. The Japanese oil dissolves in 500 volumes of 50 per cent. alcohol, whilst European oil requires 1000 volumes at least.

Pure calamus oil from any source should yield no distillate below 170°.

Traces of a crystalline compound melting at about 167°

were obtained by Schimmel from an old oil, which Soden has shown to have the formula $C_{15}H_{26}O_2$.

N. O. Liliaceæ.

Garlic Oil.—This oil is distilled from the entire fresh plant *Allium sativum*. The average yield of oil, according to Schimmel, is about 1 oz. from 1 cwt. of the plants, although Wertheim obtained 3 to 4 oz. from this quantity. The oil is a liquid possessing the characteristic unpleasant odour of garlic, optically inactive, of specific gravity 1·045 to 1·060. It was examined by Wertheim, who stated that it contained allyl sulphide and allyl oxide. The most modern and most trustworthy examination of the oil, however, is due to Semmler (*Arch. Pharm.*, ccxxx., p. 434). He states that the garlic yielded ·09 per cent. of oil of specific gravity 1·0525 at 14·5°. A small quantity of crystals was deposited when the oil was cooled in a freezing mixture. The oil contains no oxygen, and therefore no allyl oxide. When fractionated under a pressure of 16 mm., four main fractions were obtained. Fraction 1 (6 per cent.) consisted of allyl-propyl disulphide $C_6H_{12}S_2$, a bright yellow oil of specific gravity 1·0231 at 15°, and boiling at 66° to 69° at 16 mm. Its odour is that of onions. Fraction 2 (60 per cent.) consisted of diallyl disulphide, $C_6H_{10}S_2$, a light yellow oil of garlic odour, much resembling the last-named body, boiling at 78° to 80° at 16 mm., and decomposing at 150°. Its specific gravity is 1·0237 at 15°. Fraction 3 (20 per cent.), boiling at 112° to 122° at the same pressure, consisted of a body $C_6H_{10}S_3$, the exact constitution of which was not elucidated. Fraction 4 (10·5 per cent.) boiled above 122°. It contained still more sulphur, and corresponded to the empirical formula $C_6H_{10}S_4$. Semmler states that allyl sulphide, $(C_3H_5)_2S$, does not exist in the oil, as originally stated by Wertheim. He also

attributes to Beckett and Wright the statement that the oil contains a sesquiterpene, which he (Semmler) also contradicts. In this, however, Semmler is in error, as Beckett and Wright examined the sesquiterpene from oil of cloves (*Jour. Chem. Soc.*, 1876, i., p. 6), which was mistranslated into the *Jahresbericht* (1878, p. 398) as *Knoblauchöl;* hence Semmler's mistake, which is reproduced in Schimmel's report (October, 1893).

The oil has a very limited employment, and is rarely used medicinally, although it has been recommended for internal use as a tonic and stimulant to the stomach, and as a vermifuge; externally as a rubefacient. Its chief employment is for flavouring culinary preparations—a practice not in favour in England. It is worth from 12s. to 15s. per oz.

Oil of Onions is distilled from the bulb and fresh herb *Allium cepa.* The average yield of the plant is 0·05 per cent. of an acrid oil of unpleasant odour and of dark brown colour. The oil has been examined by Semmler (*Archiv Pharm.*, ccxxx., p. 443), who states that he obtained ·005 per cent. of oil, which contains no oxygen; its specific gravity was 1·041 at 9°, and its optical rotation – 5°. As it decomposes when boiled under ordinary pressure, it was fractionated at 10 mm. The chief portion of the oil consisted of a compound $C_6H_{12}S_2$, an oil of specific gravity 1·0234 at 12°, boiling at 75° to 83° at 10 mm. From the higher boiling fractions a substance was obtained, apparently identical with one of the constituents of oil of asafœtida. No allyl sulphide was found. The employment of this oil, which is somewhat disagreeable to manufacture, is quite similar to that of oil of garlic.

Allium Oil, from the fresh herb *Allium ursinum*, has a specific gravity 1·013, and contains various vinyl sulphides.

N. O. Irideæ.

Orris Oil.—Three species of the Iris are used for the preparation of this oil. These are (*a*) *Iris germanica*, common in the districts near Florence, and also found in Central Europe, Northern India and Morocco; (*b*) *Iris pallida*, found in Istria, Florence and Lucca; (*c*) *Iris florentina*, occurring on the Macedonian coast, and near the coasts of the Black Sea, and also in the neighbourhood of Florence and Lucca. The finest roots are produced in the Tuscany district, and are known as Florentine orris root, but it must be remembered that *Florentine* root is not synonymous with the root of *Iris florentina*, but embraces the three varieties, which grow to the highest degree of perfection in this district. After the Tuscany root, the Veronese is most valued. The roots, or more correctly the rhizomes, exported from Morocco and East India are of very secondary value, and do not arrive in the market in very good condition. The plant used to be left entirely to itself to grow wild, but extensive plantations are now cultivated. The plants are grown on hills, generally on sunny open spaces, or between rows of vines. A dry calcareous soil is most suitable. The plants are left undisturbed for two or three years, when the harvesting commences. Locally the plants are known as *giaggiolo*. The fresh rhizome has very little odour, and must be carefully dried before being sent away. Certain changes appear then to set in and the odour develops.

The odour of the dried rhizomes resembles the delicate violet perfume, and the powdered substance is a usual constituent of *violet powder*. The earlier application of this delicate perfume was in the form of an alcoholic extract, often known as essence of violets. But non-odorous substances are also extracted from the root by alcohol, and the odour is not so delicate as that of the carefully distilled oil.

The yield of oil is from ·1 to ·2 per cent.; but when the rhizome is treated with dilute sulphuric acid, the starch granules are broken up and liberate more essential oil, but the odour is much impaired. The essential oil obtained from the plant is of a buttery consistence, and contains certain non-volatile fatty bodies which are carried over mechanically by the steam. Flückiger, who investigated this substance, showed that it consisted chiefly of myristic acid with traces of the true volatile oil. Our present knowledge of the oil, however, is chiefly due to Tiemann and Krüger. These chemists obtained the oil by extracting the roots with ether, and steam-distilling the residue left on evaporation. The non-volatile portion contains a little myristic acid, whilst the volatile oil contains a large amount of myristic acid and its methyl ester, oleic acid, an oleic ester, oleic aldehyde, and a body which is responsible for the characteristic odour which they termed irone. This body was separated in a pure state by converting it into its phenylhydrazone and decomposing this with dilute sulphuric acid. Irone $C_{13}H_{20}O$ is an oil almost insoluble in water, readily soluble in alcohol, etc., boiling at 144° at 16 mm., of specific gravity ·939 at 20°. It is dextro-rotary. In the pure form the odour is sharp and unlike violets, but when diluted it somewhat resembles the natural violet flowers. Tiemann and Krüger then attempted to synthesise irone, believing it to be the odorous principle of the violet flower (of which so small a yield is obtained as to render an exact examination almost impossible). Whilst they did not succeed in producing irone, they obtained an isomeric body, pseudo-ionone, by condensing citral with acetone, which on heating with dilute sulphuric acid is converted into another isomer, which they termed ionone. This body is the now well-known artificial violet perfume, so extensively used in the so-called violet scent and soaps. This will be further dealt with in a later chapter, when the

chemistry of irone will also be referred to. Commercially, the aspect of orris oil is very important. Its unique delicate odour will prevent it from being replaced by the more intense but less delicate odour of ionone, and further, it forms an excellent "fixer" for this artificial perfume, so that a judicious mixture of orris oil and ionone leaves little to be desired. Its employment in fine perfumery is, and has for many years been, very extensive. A quite liquid oil, from which the inodorous solid constituents have been removed, is now on the market. According to Stead it has a specific gravity 0·949, optical rotation − 28°, and congeals at − 5° C. Schimmel & Co., however, have shown that it is dextro-rotary to the extent of about +15°.

N. O. ZINGIBERACEÆ.

Ginger Oil.—This oil is the product of distillation of the rhizome of *Zingiber officinale*, a native of tropical Asia, which is also cultivated in both East and West Indies and in Africa, and to a small extent in Australia. Possibly, also, it is found in China, although the greater part of the "Chinese ginger" appears to be the product of *Alpinia Galanga*.

The rhizomes are sometimes imported in the soft juicy condition known as "green ginger," but the ordinary ginger of commerce consists of the dried rhizomes which have been picked when the stalks have withered, and are either washed, dried and scraped (*uncoated* or *white* ginger), or merely washed and dried (*coated* ginger). Sometimes it is bleached or limed before sale. The gingers of commerce are of widely different value, according to their place of origin, and the aroma and value of the oil naturally depend to some extent upon this. The Jamaica product is most highly valued. The oil, which is obtained to the extent of about 2 to 3 per cent., is a pale yellow to dark yellow

liquid of characteristic aromatic odour, but lacking the pungency of the rhizome. Its specific gravity is from ·872 to ·885, and it is laevo-rotary – 25° to – 45°. Its refractive index is about 1·4885 to 1·4950. Very little is known of the chemistry of this oil. Thresh in 1881 published a paper on the subject, but apart from the statement that the chief ingredient of the oil is a sesquiterpene or mixture of sesquiterpenes, little information of value was given. Schimmel & Co. (*Report*, April, 1894) have examined the terpenes of the oil and have identified phellandrene and camphene amongst them. The former was identified by its crystalline nitrite and the latter by its conversion into isoborneol. According to Thresh, the English distilled oil yields the following fractions on distillation:—

	Per cent.
Below 150°	5
150°-200°	10
200°-240°	8
240°-265°	60
265°-360°	7
Residue	10

These results yield but little information, however, as decomposition goes on to a slight extent during distillation at ordinary pressures.

If the oil be fractionally distilled, the fraction 155° to 165° is found to be highly dextro-rotary, up to + 60°.

Von Soden and Rojahn have separated the characteristic sesquiterpene of this oil, which they term zingiberene. It has a specific gravity 0·872 and optical rotation – 69°. It boils at 269° to 270°. Traces of an aldehyde were also found. A small quantity of cineol, citral and borneol have also been found present in the oil. Possibly a trace of geraniol is also present.

A comprehensive examination of this oil is greatly needed.

The chief employment of this oil is for flavouring

liqueurs and other beverages, but extracts of the rhizome are preferred on account of their greater pungency.

Galangal Oil.—This oil is obtained from the rhizome of *Alpinia galanga*, a plant cultivated in China and Siam, and from which the greater part of the so-called "ginger" of these countries is obtained; possibly also from *Alpinia officinarum*. The oil is obtained by moistening the ground rhizomes with water, and after some hours distilling them with steam. The oil is of a greenish-yellow colour, with a sharp taste and pungent camphoraceous odour. The yield is from ·5 to 1·5 per cent. The specific gravity varies from ·915 to ·925, and the rotation from − 1° to − 4°. The only constituents which have been identified with certainty are cineol (eucalyptol), of which it contains a large proportion, and eugenol, which is present to the extent of 25 per cent. According to Dragendorff, the oil should not be quite soluble in an equal volume of 85 to 90 per cent. alcohol. He states that the chief adulterants are oils of pimento and cloves, which are much more soluble in alcohol. The ready solubility of samples of oil in all proportions of 80 per cent. alcohol is, therefore, probably indicative of adulteration. Oil of lemon and turpentine are also used to sophisticate the pure oil. These will be indicated by the lowering of the specific gravity and the alteration in the optical rotation. This oil is worth about four times as much as a fair quality ginger oil.

Cardamom Oil.—The oils form different kinds of cardamoms, and although similar in general properties, differ to a certain extent chemically. The seeds from which the oil is distilled are chiefly exported from South-west India and Ceylon in their pericarps, forming the cardamoms of commerce. The *British Pharmacopœia* of 1885 prescribed Malabar cardamoms, but the 1898 *Pharmacopœia* is less stringent, and there are three chief varieties agreeing with

the new description. According to the *Chemist and Druggist* (*Diary*, 1899, p. 500), the following are their chief characters:—

"*Mysores.*—Divided into rounds and longs. The former are what the *B. P.* calls 'ovoid'; they vary in length from ¼ inch to ⅝ inch (the latter 1 in 10), and have a smooth pericarp of a cream colour, due to the use of bleaching agents. Their quality is judged by their weight. Sometimes the seeds are shrivelled (unripe), so that the fruit is husky. This is not so frequent in the longs, which are simply thinner than the rounds, and are not so smooth on the surface, nor so pale, as a rule. The *B. P.* description, 'longitudinally striated,' might exclude most of the rounds, as they look smooth until closely examined.

"*Malabars.*—These are smaller than Mysores, and there is a greater proportion of seed to pericarp in them. They are fat pods, with a pointed apex. Generally pale brown or pink and longitudinally striated. Rarely more than ½ inch long. They have a full flavour.

"*Mangalores.*—These are almost globular in shape and not unlike Malabars. All three are washed or bleached before exportation.

"*Seeds.*—A goodly proportion of cardamoms come straight into the market freed from their pericarps. The *B. P.* excludes these because they are supposed to lose flavour on keeping. Wholesalers and large manufacturers use them when fresh; fine brown seed is as strong as the kind just freed from the pericarps. Grey seeds are inferior."

It is fairly certain that the plant *Elettaria cardamomum* produces most of the ordinary cardamoms, whilst the "Ceylon wilds" are the product of a variety of this plant, known as *variety β*. The majority of the cardamoms of commerce are imported from Ceylon, and may be described as *Ceylon-Malabars* or *Ceylon-Mysores*, according as they fit in with

the above descriptions. The Ceylon wilds are mostly consumed in the manufacture of a certain cake made in South Germany, and are not an ordinary article of commerce. Some confusion exists as to the botanical characters of some of these seeds, and more so as to the essential oils they yield. The oil is usually distilled from Ceylon seeds, which yield from 3 to 6 per cent. of oil. According to Weber, cardamom oil contains terpinene, and another terpene (either limonene or dipentene) and terpineol. According to Schimmel, the oil derived entirely from Malabar cardamoms (*Elettaria cardamomum*) is obtained to the extent of from 4 to 8 per cent. of the seeds used. Its specific gravity was ·943 and its optical rotation + 34° 52′. It dissolved in 4 parts of 70 per cent. alcohol. It was found to require 13·2 per cent. of potash for saponification, thus indicating a very high ester content. The esters were chiefly those of acetic acid. Whilst no terpinene was found in the oil, a considerable amount of cineol and dextro-rotary terpineol were detected. The chemistry of these oils still requires considerable elucidation. Haensel gives the specific gravity as 0·933 and the optical rotation as + 26°. Samples of oil distilled from both Malabar and Mysore (Ceylon) seeds, obtained from authentic sources by the author, showed that there was practically no difference between the two oils, although Schimmel states that Ceylon cardamom oil has a specific gravity of ·895 to ·910 and a rotation of + 12° to + 13°. It is probable that the oil from the so-called Ceylon wild cardamoms is here meant.

The Ceylon-Malabar seeds distilled by the author yielded 1·3 per cent. of oil, and the Ceylon-Mysores 2·6 per cent. Both were bright yellow liquids, whose odours were scarcely distinguishable. The specific gravities and optical rotations were as follows:—

	Sp. Gr. at 15·5°.	Optical Rotation at 16° (100 mm. Tube).
Oil of Malabar cardamoms . . .	0·9418	+40° 41′
Oil of Mysore cardamoms . . .	0·9418	+46° 39′

These figures are in fair agreement with those given for Malabar oil, but in no way resemble those quoted by Schimmel for Ceylon oil, which are difficult to understand.

The oils were soluble with a slight opacity in 40 to 45 volumes of 60 per cent. alcohol.

Little difference exists between the two oils. On distillation at ordinary pressure the oil, which is very rich in esters, in both cases decomposes partially, and a considerable quantity of free acid distils over. According to Weber (*Annalen*, 238, 89), formic and acetic acids are found in the distillate. Acetic acid is undoubtedly the chief acid constituent of the esters, but the author is unable to confirm the presence of formic acid. If it is present, it is only in faint traces. On distillation under reduced pressure the earlier fractions (the boiling point rises gradually until 50 per cent. has distilled over) contain cineol, but only to the extent of 5 to 10 per cent. of the oil. This figure is the result of an approximate estimation by means of phosphoric acid. The earlier fractions also contained one or more terpenes, amongst which was limonene. Weber states that terpinine is also present, but the author was unable to identify this hydrocarbon, nor could Schimmel find it in Malabar oil; and as it easily forms a well-defined nitrite when present, it cannot exist in an appreciable quantity. A small quantity of terpineol is present in both oils, and is easily identified by its phenylurethane. Schimmel states that it is an optically active modification. The terpineol comes over with the fraction obtained at 160 to 170° C. at 18 mm. The nature of the alcoholic constituent

of the greater part of the esters requires further elucidation. Wallach has recently identified the terpene sabinene in this oil.

In addition to the above, the following varieties of "cardamom" oil have been described: *Korarima Cardamom Oil* is the product of *Amomum korarima*. The yield is about 2 per cent., but the oil has not yet been examined.

Kameroon Cardamom Oil.—The fruits from which this oil is obtained are identical with the Madagascar cardamoms. They are derived from *Amomum danielli*. The yield of oil was 2·33 per cent., its specific gravity was ·907, and its optical rotation – 20° 34′. The oil is soluble in 7 to 8 parts of 80 per cent. alcohol. It contains cineol and possesses an odour which prevents its being employed as a substitute for the ordinary oil.

Siam Cardamom Oil.—This oil is distilled from the seeds of *Amomum cardamomum*, which are known on the market as camphor seeds on account of their camphor-like odour. Schimmel obtained 2·4 per cent., which was semi-solid at the ordinary temperature, and had an odour of camphor and borneol. In order to liquefy the oil it was necessary to warm it to 42°. Its specific gravity at this temperature was ·905, and its optical rotation + 38° 4′. It required 1·88 per cent. of KOH to saponify the esters present, and contained alcohols equivalent to 22·5 per cent. of borneol. It was soluble in 1·2 volumes of 80 per cent. alcohol. From 800 grammes of the oil 100 grammes of the solid compounds were obtained by centrifugal action. These were examined and found to consist of about equal parts of *dextro*-borneol and *dextro*-camphor.

Grains of Paradise Oil are obtained from the seeds of *Amomum Melegueta* to the extent of ·75 per cent. The odour is aromatic, but not so fine as true cardamom oil. Its specific gravity is ·894, and optical rotation about – 4°. It is soluble in 10 volumes of 90 per cent. alcohol.

Bengal Cardamom Oil is obtained from the seeds of *Amomum aromaticum*. Schimmel obtained from these 1·12 per cent. of a light yellow oil having the specific gravity ·920 and optical rotation – 12° 41′. It possessed a strong odour of cineol, and was soluble in an equal volume of 80 per cent. alcohol. The greater part distilled over below 220°. Although this oil resembles true cardamom oil somewhat, it lacks the characteristic odour of that oil, and cannot therefore be used in its place.

Turmeric Oil is distilled from the roots of *Curcuma longa*, one of the Zingiberaceæ indigenous to India, and cultivated also in China and Southern Asia, etc. The oil, which is not of commercial importance, is obtained to the extent of about 5 per cent. as a thick yellow oil of specific gravity ·940. According to Jackson and Menke (*Amer. Chem. Jour.*, iv., p. 368), it is separable by fractional distillation under a pressure of 60 mm. into three portions, the first boiling below 193°, the second from 193° to 198°, and the third forming a semi-solid residue. The chief ingredient was the fraction 193° to 198° which consisted of a nearly pure alcohol, a pale yellow oil with an aromatic smell, of specific gravity ·9016, and optical activity $[a]_d = + 33° 52'$. At ordinary pressure it boils at 285° to 290°. It appears to be an alcohol of the formula $C_{19}H_{28}O$ which has been called turmerol. Valeric and caproic acids have also been isolated. According to Suida, the principal ingredient is a body isomeric with carvone, $C_{10}H_{14}O$, but this is probably incorrect. The terpene phellandrene has been found in the oil. This oil has a characteristic curry-like odour, and is of little or no commercial importance.

Zedoary Oil, the product of distillation of the roots of *Curcuma Zedoaria*, the zedoary of commerce, is an oil of specific gravity ·990 to 1·010, occurring to the extent of from 1 to 2 per cent. in the roots. With the exception that

cineol has been identified as one of its constituents, practically nothing is known of its chemistry. It is a thick yellow oil with a camphoraceous odour, due, no doubt, to the presence of cineol.

Kaempferia Oil is the product of distillation of the roots of *Kaempferia rotunda*, a plant which was for a long time believed to be that which yielded the zedoary of commerce. This is now, however, known to be incorrect. The yield of oil is about ·2 per cent. Its specific gravity is ·890 to ·900 and its optical rotation about + 12°. If kept long, however, the oil thickens and the specific gravity increases to 0·945 or even 0·950. It contains cineol.

Hedychium Oil is distilled from the flowers of *Hedychium coronarium*. Its specific gravity is given by Schimmel as ·869 and its optical rotation as − 0° 28′. There are a large number of species of this genus, mostly natives of India, with very aromatic flowers. Practically nothing is known, however, of their essential oils. A useful *résumé* of their botanical characteristics will be found in Sawyer's *Odorographia* (second series, p. 72).

II. DICOTYLEDONS.

(A) *Monochlamydeæ*.

N. O. PIPERACEÆ.

Oil of Cubebs.—This oil, which is official in the *British Pharmacopœia*, is distilled from the fruit of *Piper cubeba* (*Cubeba officinalis*, Miq.). The cubebs of commerce are the dried unripe fruits, which resemble ordinary black pepper in appearance, except that they are rather lighter in colour; they are chiefly imported from Java.

The berries are coarsely ground and distilled with steam, yielding from 10 to 18 per cent. of volatile oil. This is of a faint greenish or greenish-blue colour, and of very characteristic and somewhat aromatic odour. The colour has been

stated to be due to copper, but this is erroneous, as the higher fractions contain a blue oil in greater or less quantity, which determines the tint of the liquid. The solubility of this oil in 90 per cent. alcohol is very variable, some oils dissolving in an equal volume, others requiring 10 volumes to effect solution. The specific gravity varies from ·910 to ·930, and the optical rotation from – 30° to – 40°, usually about – 32°. Its refractive index is about 1·4950. The chemistry of this oil is in need of further elucidation, as it is clear that there are several constituents present which have, so far, escaped identification. The terpene dipentene is present, and the sesquiterpene cadinene, probably together with another sesquiterpene. There is also present, especially in the oil distilled from old fruit, which has doubtless become partially oxidised, a small amount of the so-called cubeb-camphor. This body, $C_{15}H_{25}OH$, appears to be a crystalline sesquiterpene alcohol derived from the sesquiterpenes (or one of them) by oxidation. From a mixture of ether and alcohol it crystallises in rhombs, melting at 65° and boiling at about 245° with decomposition. The nature of the blue oil found in the higher fractions is unknown. Fractionation yields useful information in the examination of the oil, and although the quantities obtained at various temperatures are not constant, the following represents an average sample, distilled from an ordinary Wurtz flask. The oil commences to boil at about 170° to 180°, and there passes over:—

	Per cent.
Below 250°	10
250°-260°	25
260°-270°	50
270°-280°	5

These results will indicate the absence of turpentine.

Few oils have varied so largely in price during the past twenty years as this. Fifteen years ago it was worth from 40s. to 50s. per lb. To-day it can be bought of absolute

purity at about 5s. to 6s. Over-production was originally partially responsible for this, but at the same time, the use of the oil in medicine is becoming much less common than it was formerly. As a drug it is valued on account of its action on the urinary organs, but in this respect it has largely given way to santal oil and balsam of copaiba. It is employed also to a small extent to flavour certain liqueurs.

Matico Oil.—This oil is distilled from the leaves and spikes of *Piper angustifolium* (*Artanthe elongata*, Miq.), a plant indigenous to tropical America. Probably other species are sometimes used for distillation. The yield of oil is very variable, from less than ½ per cent. to 3·5 per cent. The oil is a liquid of somewhat penetrating odour, of specific gravity ·93 to 1·130, according to the species of plant used in distillation. The oil is now usually found to have a specific gravity 1·05 to 1·130 and is usually slightly laevo-rotary. It is soluble in 10 parts of 80 per cent. alcohol, and optical rotation from − 1° to + 6°. Very little is known of the chemistry of the oil. There is present a small quantity of "matico camphor," a crystalline odourless solid of specific gravity 1·080, melting at 94° and strongly laevo-rotary. Its formula is $C_{12}H_{20}O$, and it has been suggested that it is the ethyl derivative of ordinary camphor, but there is no experimental evidence in favour of this. This body seems to be generally absent from the oil distilled at the present time. Schimmel & Co. state that they have found asarone $C_{12}H_{16}O_3$ in one sample of the oil, which had the specific gravity 1·077 and was slightly laevo-rotary.

An oil has recently been examined by Schimmel which contained much asarone. A mixture of terpenes and cineol was also identified. A sesquiterpene alcohol also appeared to be present in this oil, which is possibly identical with the matico camphor which is now not always present in

normal distillates. How far differences in climate and soil are responsible for these peculiarities is not known.

The oil, which is employed in medicine to a small extent, is often adulterated with alcohol and turpentine, on account of its high price. Its commercial importance is not great.

Betel Oil is distilled from the leaves, either fresh or dried, of *Piper betle* (*Chavica betle*, Miq.). The yield is from ·5 to 1 per cent. Eykman investigated the oil some years ago and stated that it contained the phenol, chavicol (*q.v.*), several terpenes, a sesquiterpene and possibly cymene and cineol. He described it as a yellowish-green oil, with a burning taste, and peculiar, pleasant odour. It was stated by him to be laevo-rotary. Bertram and Gildemeister, however, in 1890, distilling the oil from the dried leaves, stated that the oil contained 70 to 75 per cent. of betel-phenol, which was found to be a methoxy-chavicol. They identified the sesquiterpene as cadinene. Schimmel states that the oil distilled from leaves from all sources contained this betel-phenol, and in addition the oil from Java leaves contained several terpenes and chavicol, and that from dried Siam leaves contained a sesquiterpene, and that from Manila contained betel-phenol, but no chavicol. They give the specific gravities as follows. Dried leaves, Bangkok, 1·024; fresh leaves, Java, ·958; fresh leaves, Manila, 1·044. The optical rotation is − 2° to + 3°. This oil is of no commercial importance.

Pepper Oil.—This oil is distilled from the unripe berries of *Piper nigrum*. The yield of oil is from 1 to 2·5 per cent. The oil is often of a greenish colour, somewhat resembling oil of cubebs, but with a much more pungent odour. The green colour is due to a high boiling constituent, possibly identical with that in oil of cubebs. Its specific gravity is 0·870 to 0·900 and the rotary power − 5° to + 2°. The oil was shown to consist of terpenes (chiefly phellandrene), and one

or more sesquiterpenes. An oil is also obtainable from the long pepper, *Piper longum*. This pepper yields 1 per cent. of a thick pale greenish oil, of specific gravity ·861, boiling chiefly between 250° and 300°.

A *Pepper Oil* is obtained from the fruits of the Javanese plant *Piper Lowong*, also known as "false cubebs". The oil obtained by direct distillation of the powdered fruits with steam has a specific gravity of about ·860, whilst that obtained by distilling the ethereal extract has the high specific gravity ·925. A sesquiterpene appears to be present, and a crystalline body melting at 164°, which is probably a sesquiterpene alcohol.

N. O. CANNABINACEÆ.

Oil of Hops.—This oil is distilled from the flowers of the ordinary hop, *Humulus lupulus*, which yield from ·3 to 1 per cent. The oil glands are situated under the scales of the flowers (catkins); these grains or glands can be separated from the flowers, and are known in commerce as lupulin. The quality of the oil is, of course, dependent on the state of the flowers, and when the crops have had to be "sulphured," the oil obtained from the flowers is less valuable and contains traces of sulphur. The pure oil has a pale yellow to faint green tint, but can be obtained colourless by rectification. It has a penetrating hop odour. The specific gravity usually lies between 0·850 and 0·880, but sometimes is as low as 0·840. The oil is usually dextrorotary, but seldom exceeds + 1°. Several chemists have investigated this oil. It is not soluble in 90 per cent. alcohol as a rule, and often not in 95 per cent. alcohol. In 1822 Payen and Chevalier stated that there were at least two bodies present. Wagner in 1853 obtained a terpene boiling at 175° and an oxygenated body which yielded valeric acid on oxidation. Personne (*Jour. Pharm.*, xxvi., p. 241, and xxvii., p. 22) obtained a dextro-rotary terpene of specific gravity ·888.

The most modern and reliable investigation, however, is due to Chapman. Four samples of authentic origin gave the following figures:—

	Specific Gravity at 15°.	*Rotation* [α]$_D$.
1	·8802	+ 0·41′
2	·8662	+ 0·58′
3	·8771	+ 0·50′
4	·8743	—

All these samples were free from sulphur and neutral to litmus. No ketones or aldehydes were detected in the oil. A prolonged series of fractionations at 60 mm. pressure yielded the following fractions: (1) 89° to 91°; (2) 145° to 150°; (3) 163° to 168°; (4) 168° to 173°. The first and fourth were the main fractions, the second and third being very small. Fraction No. 1 was a colourless oil, practically unacted upon by sodium. When distilled from this metal, it boiled at 86° to 89° at the same pressure. Under ordinary pressure it boiled at 166° to 171° almost entirely, but towards the end, the temperature went up to 250°, due to polymerisation of the original substance. The specific gravity at 20° was found to be ·799 and the rotation − 0·56′. It is clear that this body is not a normal terpene, and Chapman's experiments lead him to consider it as a mixture of tetrahydrocymene, and one of the so-called "olefenic terpenes," bodies as yet but little understood. Fraction No. 2 was a liquid of specific gravity ·885, and may be geraniol. Fraction No. 3 was a mixture of 2 and 4. Fraction No. 4 was found to be a sesquiterpene, to which the name humulene (*q.v.*) was given. The same observer has also published figures for hop oils obtained from different sources as follows:—

		Specific Gravity.	*Rotation.*
Bavarian hops	1894	0·8676	+ 0° 30′
„	1901	0·8403	− 0° 08′
Californian hops	1899	0·8639	− 0° 20′

On distilling one of these oils he obtained again the "olefenic" terpene above referred to, and linalol, together with an acid $C_9H_{18}O_2$ (probably isononylic acid) in the form of esters. Dipentene was also detected and probably esters of geraniol. The sesquiterpene humulene and the olefenic terpene make up more than 80 per cent. of the oil. Schimmel & Co. have detected gurjun oil as an adulterant of this oil.

For further details of the chemistry of this body, which constitutes the greater part of the oil, see the original papers (*Chem. Soc. Proc.*, 1893, p. 177, and *Jour. Chem. Soc.*, 1895, pp. 54 and 780, and 1903, p. 505). This oil, which is very expensive, is used to some extent in the brewing industry, both to add flavour to beer and to give a good odour to poor and damaged hops.

Hemp Oil.—The flowers of *Cannabis sativa* yield about $\frac{1}{10}$th per cent. of volatile oil of specific gravity about ·930. It is laevo-rotary to the extent of about − 10° to − 12°. The oil appears to consist entirely, or nearly entirely, of sesquiterpenes and terpenes.

Indian Hemp Oil is obtained by subjecting the flowering twigs of *Cannabis Indica* to steam distillation. According to Valente the resulting oil is of thin consistency, and possesses an agreeable aromatic odour. It boils between 248° and 268°. Its specific gravity is about ·930, and optical rotation − 10°, and it appears to consist chiefly of a sesquiterpene, which has been named cannibene.

Vignolo obtained an oil by distilling the female flowering plant, of similar boiling point, and of optical rotation − 18°. Wood, Spivey and Easterfield isolated from the resinous extract an oil of the formula $C_{18}H_{24}O_2$, which is resinous at ordinary temperatures, and boils at 265°. Its specific gravity is 1·0424 at 18°. It has been termed cannabinol. They also found a slightly laevo-rotary terpene (?), of specific gravity 0·819 and boiling at 160° to 180°. They found that the ses-

quiterpene distilled at 258° to 259°, and had a specific gravity 0·898 at 18° and a rotation of – 8·6°.

N. O. Myricaceæ.

Bayberry Oil.—The leaves of *Myrica cerifera*, the bayberry or the wax myrtle, yield about ·02 to ·05 per cent. of an essential oil of specific gravity about ·885 and optical rotation – 5°. The leaves of the bog myrtle, *Myrica gale*, also yield a small quantity, under 1 per cent., of oil of agreeable odour. Its specific gravity is about ·870. It contains a large quantity of stearoptene, and solidifies at about 11°. The chemistry of these oils is practically uninvestigated. (These plants must not be confused with the true myrtle, *Myrtus communis*, which will be referred to later.)

Sweet Fern Oil.—The leaves of *Comptonia asplenifolia*, another plant of this natural order, yield about $\frac{1}{10}$th per cent. of an essential oil of specific gravity ·926, congealing when cooled.

N. O. Salicineæ.

Poplar Oil.—The young buds of the black poplar, *Populus nigra*, yield from ·3 to ·6 per cent. of oil of a pale yellow colour somewhat recalling the odour of chamomiles. Its specific gravity varies from ·900 to ·905. Its optical rotation is + 1° to + 6° and its ester number about 15. Picard gives ·9002 as the specific gravity of a sample he examined, and stated that it consisted chiefly of a hydrocarbon $C_{20}H_{32}$, was dextro-rotary, and boiled at 260°. Fichter considers, however, that it consists chiefly of the sesquiterpene humulene, and another sesquiterpene not yet identified.

N. O. Chenopodiaceæ.

Chenopodium Oil.—This oil is also known as American wormseed oil. It is distilled from both the fruit and the whole herb of *Chenopodium ambrosioïdes*, var. *anthel-*

minticum, the fruit yielding about 1 per cent., and the herb ·3 per cent. of oil. The specific gravity of the fruit oil is about ·975, and of the herb oil about ·900. According to Schimmel (*Report*, 1893), samples of fruit oil from absolutely reliable sources have a specific gravity of about ·970, and are soluble in 10 volumes of 70 per cent. alcohol. The fruit oil is laevorotary, from − 5° to − 18°. The herb oil has an odour recalling trimethylamine, but nothing definite is known of its chemistry. Oil from seeds only has a specific gravity about 0·900; that from the leaves, 0·880. It is probable that this oil contains limonene and an alcohol of the formula $C_{10}H_{16}O$.

N. O. Laurineæ.

Cassia Oil.—This oil is distilled from the leaves, twigs and other parts of the plant *Cinnamomum cassia*, which is probably a native of Cochin China, but which is chiefly cultivated in China proper, the three chief districts being Taiwu (*Lat.* 23° 34′ N., *Long.* 110° 18′ E.), in the Kwangsi province; Lukpo (*Lat.* 23° 6′ N., *Long.* 112° 24′ E.), and Loting (*Lat.* 22° 52′ N., *Long.* 111° 8′ E.), both in the Kwangtung province. Much confusion and mystery existed till recently in regard to the exact botanical source of the plant and the nature of the oil and the methods of its distillation, etc., which were largely brought about by the shameful adulteration by the Chinese. The following details given by actual observers will give the most reliable information on much affecting these questions. In a *Report on a Journey to Kwangsi*, by H. Schroeter, 1887, the writer says:—

"The shrubs destined for the production of the *Cassia lignea* proper are partly stripped during the summer months of their minor branches and exceptionally juicy leaves. They are then conveyed in huge bundles into the valley, where they are boiled in large vessels. From the aromatic juice thus obtained the esteemed cassia oil is recovered by means

of a most primitive distilling apparatus. As the Li-kin stations on the road to Canton levy an excessive duty upon the oil, in addition to that exacted by the Imperial Customs, the oil is carried in tins across the hills to Pakhoi and thence transported to Hong-Kong, *viâ* Macao, instead of reaching Canton by the waterway, intended by nature for its conveyance."

These statements are in agreement with those contained in a report presented to the Hong-Kong Government by Mr. Charles Ford, which will be found reprinted in the *Journal of the Linnæan Society*, December, 1882, and in which much valuable information is given. More recently (1895), Messrs. Siemssen & Co. of Hong-Kong, on whose behalf Herr Schroeter's visit was made, sent a representative, Mr. Struckmeyer, to the Loting-Chow districts, in company with the German consul, Dr. Knappe. The report of these travellers is sufficiently interesting to warrant its reproduction here. For it, the author is indebted to Messrs. Schimmel & Co. It reads as follows:—

"We embarked on the right bank of the West river, opposite Tack-Hing-Chow, at six A.M. on the 15th of December, 1895. We left there our large boat and went to a place with extensive matting factories, located on the Loting-Chow or Lintau river, arriving there about half-past two o'clock in the afternoon. Next morning we continued our march to Loting-Chow, under the guidance of a Chinese, a manager of one of the largest matting establishments in Lintau. We were attended by a servant of the consul, who also served as interpreter, and by several Chinese coolies. After a brisk march we took up our quarters in a small Chinese temple, and made strolls through the city, which, although small, seems to be a busy trading place. Loting-Chow is pre-eminently a centre for all the products of the cassia tree, and for firewood to be shipped thence to Canton and Macao.

"The cassia plantations are still further inland, and we had to defer visiting them until the next day, because they were too far off, according to our informants in Loting-Chow. They proposed, however, to accompany us the following day to cassia plantations as well as to a distillery. During the afternoon we visited a dealer in cassia oil, the only one in the place, he pretended. Subsequently, on our return, we ascertained this statement to be false. At first he was very reticent, but subsequently yielded to some pressure. He possessed a separating funnel, a syphon, test-tubes, etc., as recommended by Messrs. Schimmel & Co. in Leipzig, and pretended to examine all oils offered to him for sale, because he had been condemned, as he said, to $900 damages for inferior cassia oil sold by him some five years ago. He assorts the commercial oil into four to five grades, but deals only in the three best qualities, unadulterated in his opinion. He had in stock but a small quantity of the best oil, and gave us small specimens of three kinds of his oil, of which I shall treat more fully further on.

"Although everything was arranged for the next day with our Chinese guides, we had to face considerable difficulties. During the evening we were informed that a certain 'Mr. Wong' (who never appeared in person) had arrived from the interior, and reported that a visit to the cassia plantations would be of no use, and that it would no be possible to inspect any distillery, because some children had been instructed by thieves to steal the leaves from the cassia trees, and that in consequence a brisk contest between the owners and the thieves was in progress. Besides, it was claimed that only one distillery existed, at a distance of 20 Lis (about 8½ miles), and that this was not in operation in consequence of the disturbances. This wondrous story, and the circumstances under which it was imposed upon us, convinced us that it was an impudent lie, or, at best, an

absurd exaggeration. The more they tried to dissuade us from continuing our trip, the more we persisted upon the realisation of our plan. Finally the Lintau Chinaman volunteered to accompany us to the plantations, but would not make any promise in regard to visiting any distillery. The departure was fixed for six o'clock the next morning. We were in a peculiar position, since our interpreter also appeared to antagonise our aims; nor had we any time to lose in order to comply with all other arrangements of our expedition.

"The next morning, 17th December, we and our men were ready at six o'clock, but the two Chinese failed to appear, although we had requested them several times to hurry. We were waiting with our attendants in front of the temple when messengers brought the idle excuse that the two Chinese had not yet received their breakfast, and that no carriers for our baggage could be obtained. At a quarter to eight we sent word that we would start without guides, and when they caught up with us at ten o'clock we paid no attention to them.

"We finally succeeded in inducing one of the many onlookers to guide us to one of the distilleries. The march went on very slowly, and the actions of our interpreter led us to foresee further intrigues. As on the previous day, our route passed through a hilly country with numerous side valleys and little ravines. After having passed a number of hills covered with young cassia trees, we reached a distillery by ten o'clock, but found out that it was not in operation. We were again told that this was the only distillery in the neighbourhood. But as luck would have it, during our brief stay a small trader appeared upon the scene and offered some thick cassia bark for sale. By small purchases and promises we succeeded in inducing the man to lead us to another distillery, and one in operation.

"We returned the same way by which we had come, and at noon-time arrived at a distillery in full operation. It was a little off the road, but was much nearer to our starting point in the morning than the distillery to which we had been led at first. We met with a very kind reception by the owner and his employees, and they readily gave us any desired information. We ascertained that about twenty distilleries existed in this immediate neighbourhood, and that most of them at the time were in full operation. We subsequently found out on our return to Canton that a few slight disturbances had occurred in the cassia districts, but the fact remained that we had been treated to absurd stories and gross lies, probably at the instigation of some dealers in Loting-Chow.

"The distillery, like all others, is located in a ravine abounding in springs which furnish an ample supply of water for coolers. The distillery with all its arrangements closely resembles the one which some time ago was described and illustrated in one of the Reports of Messrs. Schimmel & Co.

"An iron pan is securely placed in a brick hearth with a large fire-place; upon this pan a large wooden cylinder lined with sheet iron is placed, upon whose upper rim a large cover of strong sheet iron rests. The space between the cylinder and the cover, around the rim, is made tight by strips of moist cloth or rags. Around the lower side of the cover there runs an outer groove for gathering and drawing off the water serving for cooling, and a narrow interior groove for collecting the distillate containing the essential oil. This distillate passes into tin cans and the oil collects at the bottom.

"At each charge of the cylinder, about 1 picul of leaves and twigs and 250 catties (= 2½ piculs) of water are employed; the water used is mostly from preceding distillates. The distillation lasts about two and a half hours.

"The yield of one such charge, when consisting of leaves

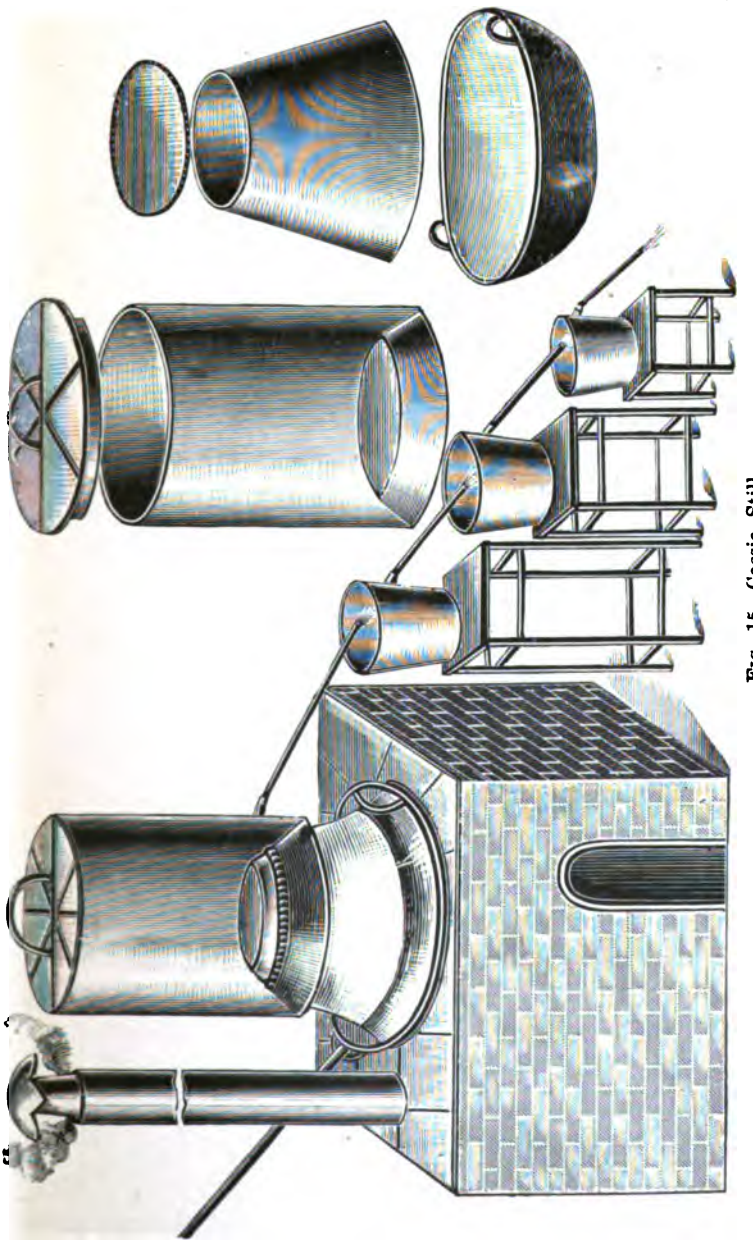


FIG. 15—Cassia Still.

only, is 1½ to 2 taels, and when consisting of 70 per cent. of leaves and 30 per cent. of twigs, 2½ to 3 taels of oil.[1] The oil obtained from leaves alone is in general the superior one.

"With a still of this capacity, as much as 50 catties of oil are obtained per month, or 3 to 5 piculs per year. The festivities connected with the Chinese New Year cause an interruption of the distillation for one or even two months. The quality of the oil depends upon the material used for distillation. Both too old and too young trees furnish leaves less rich in oil; large leaves are better than small, young ones; this explains the fact that the twigs and leaves gathered in spring and in winter yield an inferior oil to those gathered in midsummer and in autumn.

"The distiller who furnishes us this information claims to produce but 1 grade of oil, using 70 per cent. of leaves and 30 per cent. of twigs. A specimen, marked A, was taken by us from the apparatus. The tin can contained but a small amount of oil resting under the water, and the sample, collected in a rather primitive way, contained some water. On standing, some drops of water separated at the top of the slightly yellow oil. It was subsequently examined by Mr. E. Niedhardt in Hong-Kong with the following result:—

"Specimen A (1895). A turbid liquid, which on standing separated into two layers, the upper one water, the lower one cassia oil of a light Rhine wine colour.

Consistency: very limpid.
Odour: the true oil of cassia, somewhat smoky.
Taste: the same.
Spec. grav.: 1·059.
Residue of distillation: 3·75 per cent.; resinous, sticky.
Cinnamic aldehyde: 86 per cent.
Solubility in alcohol 80 per cent.: complete.
Solubility in solution of sodium salicylate: complete.
Reaction with lead subacetate: no turbidity.

[1] 16 Taels = 1 Catty = 605 Grammes; 1 Picul = 60 Kilos 500 Grammes.

"The result of this investigation indicates that a rather large proportion of twigs seems to be required to materially reduce the quality of the oil. Perhaps twigs too old and too thick have a detrimental effect upon the quality of the distillate.

"The oily water, as collected during the process of distillation, is milky. Specimen B represents this water as separated from the oil and mixed with Specimen A.

"Specimen C represents the ready oil as our distiller sends it to Loting-Chow for sale. The specimen was taken from a tin can by ourselves.

"For these samples we were charged in proportion to the regular price of $600 per picul.

"The distillers generally purchase the leaves and twigs and carry on the distillation on their own account; occasionally they rent their stills to the owners of the raw material, mostly planters, or they run their stills on the latter's account in return for a compensation.

"In Loting-Chow we obtained two more samples of commercial oil. Specimen D was said to be a good oil of prime quality obtained from old leaves and commanding a price of $600 per picul. It did not change when brought into contact with water, but separated into smaller or larger globular masses, showing a few oil drops on the surface. It was of a light colour.

"Specimen E, said to be distilled from young leaves; price $580 per picul. It showed in water a more compact mass with a thin, transparent surface, and more oil drops on top of the water.

"Specimen F was said to have been obtained from old and young leaves and to have been adulterated with kerosene, and therefore to be of no use to the dealer; price $550. When brought into water, this oil formed a compact mass with a thick surface, partly of a whitish and striped appearance.

Colour rather dark. The dealer stated that he had showed us this oil only as a specimen of adulterated oil, that he kept it only as a sample and that he had only a small amount of it. Consequently he could only sell us such a small sample.

"The adulteration is charged by every one to somebody else. We found no suspicious material in the distilleries, there is an abundance of pine leaves growing in the region, but their admixture to the cassia leaves was peremptorily denied; nor did we find any such admixture in the contents of the still examined by us. Although a few distillers may be guilty of dishonest practices, there is no reason to assume that the majority resort to deliberate adulteration by the admixture of foreign matter to the cassia leaves and twigs. On the other hand, we may conclude from the existence of adulterated oil in Loting-Chow, and from our examination made there, that the sophistication ought not to be imputed exclusively to the Chinese of Macao and Hong-Kong, if at all. The fact is, before the oil is sold to the foreign exporters, it comes from an extensive district and passes through so many hands that it is impossible to determine where and how it is actually adulterated. In Loting-Chow it was alleged that most adulterations are committed in the province of Kwang Si, where ten or even more qualities of cassia oil can be had.

"The question may here be raised whether the present methods of examination suffice to detect the most artful and subtle adulterations, as also whether the Chinese really possess the requisite knowledge and skill for such refined forms of sophistication.

"Sample A bears sufficient evidence that excellent oil can be, and is, produced. This detailed account, however, may indicate what difficulties the foreigner has to meet with when trying to get at the bottom of facts.

"Incidentally it may be added that the residue of the

leaves and twigs, after having been dried, is used as burning material. The remaining ashes are subsequently extracted by hot water, and a kind of potash called Kamalni is obtained therefrom.

"Consul Dr. Knappe has forwarded a collection of the samples A, B, C, D, E and F and an elaborate report to the Foreign Office in Berlin. Sample A is the only one which we had examined in Hong-Kong."

Much credit is due to Messrs. Schimmel & Co. for the thorough way in which they have dealt with the cassia oil question, not only in connection with their efforts to combat the enormous adulteration practised by the Orientals, but in regard to their investigations of many of the difficult points existing in reference to this oil. They have obtained specimens of raw materials of various parts of the plant and examined the oils yielded by them. The results of their investigations are summarised as follows:—

"*Cassia Budsticks.*—Small, thin stalks, about 1 mm. thick and 5 mm. long, which possess a strong and pure cinnamon taste. Six hundred and fourteen kilos distilled by us yielded 10 kilos 120 gr., or 1·64 per cent. of a beautifully bright oil with excellent sweet taste, indicating a high percentage of aldehyde.

"We determined the specific gravity to be 1·0463, the aldehydic contents 92 per cent.

"*Cassia Leaves.*—The dried, leather-like leaves of the cassia plant with the strong petioles and small twigs. On mastication of leaves and petioles separately, both communicated a faint but pure taste of cinnamon, whilst the twigs exhibited strong cinnamon taste.

"In order to obtain exact results we caused a certain quantity of the material to be sorted into leaves and stalks. One hundred kilos material yielded—

Leaves	85 kilos
Small twigs . . .	15 ,,

"On distillation the leaves yielded a beautiful, sweet tasting oil, with specific gravity 1·056 at 15° C. The aldehydic contents were determined as 93 per cent.

"The thin twigs showed a less percentage of essential oil than the leaves, but this possessed a similar sweet taste to the oil from the leaves. The specific gravity was 1·045 at 15° C. The aldehyde amounted to 90 per cent.

"The following parts of the cassia plant have been distilled by us with the appended results :—

1. The Cassia bark (the *Cassia lignea* of commerce).
   Yield of essential oil : 1·5 per cent.
   Aldehyde in oil : 88·9 per cent. Specific gravity 1·035.
2. The Cassia buds (the *Flores cassiae* of commerce).
   Yield of essential oil : 1·550 per cent.
   Aldehyde in oil : 80·4 per cent. Specific gravity 1·026.
3. Cassia budsticks.
   Yield of essential oil : 1·64 per cent.
   Aldehyde in oil : 92 per cent. Specific gravity 1·046.
4. Cassia leaves, leafstalks and young twigs mixed.
   Yield of essential oil : 0·77 per cent.
   Aldehyde in oil : 93 per cent. Specific gravity 1·055.

"Nos. 1 and 2 are completely excluded as raw materials for the preparation of cassia oil on account of the price.

"No. 3 is also out of the question, because the value, about $4 per picul, is still higher than that of broken cassia and because the yield would not be sufficient.

"It can, therefore, be assumed with safety, that the cassia oil of commerce is distilled in China from the leaves, leafstalks and young twigs of the cassia plant, probably together with various refuse products worthless for other purposes."

The ordinary commercial oil of cassia, which is imported from Hong-Kong, etc., in cases containing lead vessels, each holding about 16½ lb., may be regarded as distilled chiefly from the leaves and twigs. The grosser adulterants, which are far less common to-day than they were a few years ago, are colophony, petroleum and fatty oils. Low grade oils are

found in commerce, which have not, so far, been positively ascertained to be adulterated. Possibly they are the product of a variety of the plant, or they may be adulterated with some oil we do not yet know of. On the markets this oil is sold entirely on a guarantee of its content of cinnamic aldehyde, and many oils of, say, 70 to 75 per cent. are undoubtedly oils of higher grade reduced with resin or resin oil.

The main constituent to which the odour of this oil, and of oil of cinnamon is chiefly due, is cinnamic aldehyde. Small quantities of cinnamic acid, its oxidation product, are naturally found in the oil, the amount varying according to its age. A terpene, a compound of cinnamic and acetic acids, and cinnamic acid esters, also exist in very small quantities. A stearoptene was also found in this oil in 1850 by Rochleder. According to this chemist its formula is $C_{28}H_{29}O_5$. But a recent investigation by Bertram and Kursten shows that it is *ortho*-methyl-coumaric aldehyde $C_6H_4(OCH_3)(CH:CH.COH)$. The oil when pure should have a specific gravity of from 1·050 to 1·065. Its refractive index is from 1·5850 to 1·60. Its optical activity should be almost *nil*, never more than 1° either way. It should dissolve completely in 2 volumes of 80 per cent. alcohol and usually in 3 to 4 volumes of 70 per cent. alcohol, a characteristic which is interfered with by adulteration with colophony, petroleum, or gurjun oil. The following rough method gives an approximate estimate of the amount of adulteration, if this is colophony, heavy petroleum oil or a fixed oil. Weigh 50 grammes of the oil into a small Wurtz flask, and connect in the usual way to a condenser, and gradually heat with a naked flame. The oil commences to boil at about 210°, and the bulk distils over between 240° and 260°. When the thermometer rises to 280° and white vapours rise the distillation is stopped.

On cooling the flask (whose weight is known) its contents are weighed; the residue should not exceed 10 per cent.—it

is seldom more than 8 per cent.—and should not solidify. Over 10 per cent. residue indicates adulteration, and if this residue solidifies colophony is present. The most important method of examination, however, is the determination of the percentage of cinnamic aldehyde, and upon this percentage commercial oils are always sold on the market. In this process the following details should be observed. Ten c.c. of the oil are run into a Hirschsohn flask (capacity about 100 to 150 c.c., with a neck about 5 inches long and $\frac{1}{4}$ inch in diameter, graduated in $\frac{1}{10}$th c.c.). The flask is then filled about three-quarters full with a 30 per cent. solution of sodium bisulphite, and the whole well shaken. The flask is then placed on the water bath for several hours with occasional shaking, until the precipitated compound of the aldehyde and bisulphite is completely dissolved, and only a clear oil floats on the surface. Bisulphite solution is then carefully poured in until the oil is driven up into the neck, and when it has attained the temperature at which the oil was measured, the amount is read off. This gives the percentage of non-aldehydic constituents, the difference being returned as cinnamic aldehyde. Pure oils should not give much less than 75 per cent. of aldehyde, the best oils yielding 80 to 85 per cent., or occasionally even higher. Strictly speaking, these percentages are by volume, but the errors of reading the result, and those due to solubility of the non-aldehydes in the aqueous liquid render any correction for the specific gravity of the constituents unnecessary in practice. Care must be taken that every particle of the aldehyde compound is dissolved, as otherwise the reading of the oily layer will be obscured, and a serious error may be introduced. If the precipitate does not dissolve after standing three hours in the water bath with repeated shaking, the presence of solid resin may be inferred, and the estimation of the aldehyde in this way, with accuracy, is then impossible. Hirschsohn recommends shaking the oil in a graduated

tube with three times its volume of light petroleum ether. A diminution in volume of the oil indicates petroleum, resin, or fatty oils (except castor oil). An increase in volume of the oil indicates castor oil. The petroleum layer is then shaken with copper hydroxide. A blue solution indicates copaiba or resin.

Hanus publishes a new method for the determination of cinnamic aldehyde in cassia and cinnamon oils (*Pharm. Central.*, 1904, 37) depending on the combination of the aldehyde with semioxamazide. Ten grammes of finely powdered hydrazine sulphate are dissolved in a solution of 9 grammes of caustic soda in 100 c.c. of water, and the alkaline sulphate produced is precipitated by the addition of 100 c.c. of alcohol. After filtration the solution is warmed, 9 grammes of oxamæthane are added in small portions, the whole warmed for half an hour and allowed to cool. The azide separates in crystalline tables, and these are separated and recrystallised. To estimate the aldehyde by means of this reagent, a small quantity, not more than 0·2 gramme, of the oil is well shaken in 85 c.c. of water, and about 0·35 gramme of semioxamazide in 15 c.c of hot water is added and the whole well shaken. After five or ten minutes the compound begins to be precipitated, and after standing twenty-four hours can be collected on a Gooch filter, washed with cold water, and dried for a few minutes at 105°. The amount of the precipitate is multiplied by 0·6083 to obtain the amount of aldehyde. The constitution of the semioxamazone of cinnamic aldehyde is $NH_2 . CO . CO . NH . N : CH . CH : CH . C_6H_5$.

This oil is an article of great commercial importance, and finds a very extensive employment in perfumery. Its odour closely resembles that of cinnamon, but it lacks the delicacy of the latter, to which it is often fraudulently added. Pure cinnamic aldehyde or "synthetic cassia oil" is now an article of commerce. It is readily formed by the action of sodium

ethylate on a mixture of benzoic and acetic aldehydes. Whilst it possesses the characteristic *cassia* odour to a marked extent, there is nothing else present to in any way modify that odour, in the way that the other constituents of cassia oil do. It may be described as having a stronger but cruder odour than the natural oil. An objection to some of the commercial aldehyde is that it contains traces of chlorine compounds, introduced during manufacture, which materially depreciate its odour value. Chlorine free cinnamic aldehyde can, however, now be easily obtained. Its value is very similar to that of pure cassia oil of good quality.

Cinnamon Oil.—The cinnamon oil of commerce is understood as the product of distillation of the bark of *Cinnamomum zeylanicum*, the Ceylon cinnamon, a native of that island. The leaves and root bark also yield essential oils, the former of which is of considerable importance commercially. The cinnamon tree is a small evergreen tree with shining leaves and panicles of greenish flowers, of somewhat unpleasant odour. It is extensively cultivated in Ceylon, from which nearly all the bark of commerce is obtained. It is also grown in India, Mauritius, the Seychelles and Jamaica, but Ceylon is responsible for practically the whole of the cinnamon used. Several varieties are cultivated, but whether they are merely the same plant slightly modified by the influence of soil, etc., or not, is uncertain. The south-west of the island in the Colombo, Negumbo and Matura districts produce the majority of the bark, and the famous "cinnamon gardens" of Colombo, which occupy a considerable space, form one of the great attractions to the island. The age of the tree, the care devoted to its cultivation, and the time at which the bark is gathered largely determine the value of the product. The appearance and size of the "quills," together with their odour and flavour, determine their value on the market. The small fragments or chips and the bark of inferior quality are used

in Ceylon for distillation, and also form the chief material from which the oil is distilled in England. The oil distilled in Ceylon is usually obtained by macerating the fragments of bark in sea-water or strong brine for two or three days and then subjecting them to distillation. The yield is from ·5 to 1 per cent. The majority of that exported, however, is not genuine. Either the leaves are added to the bark when distilled, or cinnamon leaf oil is added to the oil after distillation. The important difference between the two oils is that the bark oil owes its characteristic odour to the cinnamic aldehyde it contains, whilst the leaf oil contains only traces of that body; the chief constituent of the latter oil is eugenol, the characteristic phenol of the oils of cloves and pimento.

The more delicate odour of cinnamon oil causes it to be preferred to cassia oil in England, whilst the stronger and coarser odour of the latter, together with its much lower price, gains for it preference in many parts of the continent. Cinnamon oil is worth eight to ten times as much as cassia oil.

The pure bark oil has a specific gravity of 1·020 to 1·035, rarely exceeding this, though Schimmel & Co. state that they have distilled an oil which had a specific gravity 1·038. Adulteration with the leaf oil or with clove oil increases this figure. The oil is optically inactive, or at most laevo-rotary to the extent of – 1°. The ascertained constituents are the terpene phellandrene, cinnamic aldehyde, and eugenol. The cinnamic aldehyde is estimated as described under *Cassia Oil*, and should never be less than 60 per cent. The *British Pharmacopœia*, in which this oil is official, gives the following limits: specific gravity, 1·025 to 1·035; cinnamic aldehyde at least 50 per cent.; should not yield a decided blue colouration with ferric chloride solution. Adulteration with much leaf oil causes the characteristic blue colour given by eugenol and ferric chloride to be developed. The amount of eugenol

estimated as described under oil of cloves, should not exceed 8 per cent. Normal oils contain from 70 to 77 per cent. of cinnamic aldehyde and from 4 to 8 per cent. of eugenol. An oil with over 80 per cent. of cinnamic aldehyde is probably adulterated with the synthetic aldehyde.

Schimmel & Co. have examined this oil fully. In the early fractions obtained by distilling *in vacuo*, they found methyl-*n*-amyl-ketone $C_7H_{14}O$, benzaldehyde, and traces of furfurol. The terpenes pinene and phellandrene and the hydrocarbon cymene were also isolated in small amount. Nonyl aldehyde $C_9H_{18}O$, hydrocinnamic aldehyde and cumic aldehyde are also present, as well as small amounts of linalol and linalyl isobutyrate, and in the high boiling fractions the sesquiterpene caryophyllene.

When the addition of synthetic cinnamic aldehyde is suspected the oil should be examined for traces of chlorine, which will be present if the cruder varieties of that body have been used.

Keimatsu has examined a sample of Japanese cinnamon oil, distilled from the leaves, trunks and roots of *Cinnamomum Loureirii*. From the leaf oil he isolated citral as the principal constituent, with small quantities of eugenol. From the trunk oil he isolated cinnamic aldehyde and a little eugenol; and from the root oil, cinnamic aldehyde, camphene, cineol and linalol. This oil has been described as oil of Nikkei.

Cinnamon leaf oil is also largely used for perfumery and other purposes. The yield is from 1·5 to 2 per cent. of a slightly optically active oil of specific gravity 1·045 to 1·060. It was examined in 1855 by Stenhouse, who stated that it consisted chiefly of eugenol (eugenic acid) and a hydrocarbon, with traces of benzoic acid. Weber (*Arch. Pharm.*, ccxxx., 232) confirmed these results in general, but could find no trace of benzoic acid. A very small quantity of cinnamic

aldehyde was, however, found. The content of eugenol is usually from 75 to 85 per cent.

The root oil has been stated to contain eugenol, safrol, benzaldehyde and benzoic esters, but the authenticity of the sample examined is doubtful. The inhabitants of Ceylon obtain from the roots a camphor-like mass, which is made into candles and burnt at festivals. Probably the chief constituent of true root oil is camphor.

Sassafras Oil.—The ordinary oil of sassafras is distilled from the root of *Sassafras officinale* (*Laurus sassafras* of Linnæus), a native of North America. The tree is one of the most widely distributed in the continent, being found in Canada, in all the States east of the prairies beyond the Mississippi, and in Mexico. In Canada it seldom exceeds 30 feet in height, but in the south, especially in Virginia and the Carolinas, it reaches nearly 100 feet in height. The root bark (except the outer layers) is the most aromatic portion of the plant, and from this, as well as the wood, the essential oil is distilled. The roots may be dug out at any season, but those dug when the sap is not rising yield the highest percentage of oil. Some of the large roots weigh nearly half a ton, but the smaller roots are most valued on account of their higher yield of oil. The typical distilleries in the neighbourhood of Baltimore use wooden tanks as stills. These are made of kiln-dried pine, and consist of wooden boxes built up of staves, with a pierced false bottom. The head is provided with a trap-door for filling by, and a large door is fitted to the bottom of the tank, for the purposes of emptying. To the upper part of the tank is fitted a copper head, leading to a condensing coil immersed in cold water. Steam at from 40 to 60 lb. pressure is admitted between the true and false bottoms. The stream of condensed products issuing from the pipe is caught in a copper funnel with a very long spout which reaches nearly to the bottom of a 20-

gallon copper vessel. The oil being heavier than water collects at the bottom, leaving the water to flow away at the top of the vessel. A charge of 10 tons requires about two days to exhaust, and yields about 10 gallons of oil. In parts of Pennsylvania and New Jersey a number of small isolated distillers, often coloured men, carry on a remunerative business in this oil. A most primitive still is used, consisting merely of a barrel with its head luted on, and its bottom pierced and standing on a steam generator. A natural elbow-shaped branch perforated throughout serves to carry the distillation products to a metal tube placed in a trough of running water. The condensed products are then separated in the usual way. Although the yield of oil is much lower than when distillation is effected in modern apparatus, the process is a payable one, as the capital necessary for such primitive distilleries is very small. Properly treated, as much as 8 per cent. of oil can be obtained from the root bark. Two samples of oil, one from the root bark and one from the wood, were distilled by Schimmel & Co., and had the following characteristics:—

	Yield.	*Specific Gravity.*	*Rotation.*
Bark . .	7·4 per cent.	1·075	+ 3° 16′
Wood . .	·9 „	1·075	—

The limits allowable are 1·065 to 1·095 for specific gravity, and + 1° to + 4° for the optical rotation. It is soluble in 1 to 2 volumes of 90 per cent. alcohol and has a refractive index about 1·5275. The earliest chemical investigation of the oil was by Grimaux (*Comptes Rendus*, 1869, p. 928), who stated that it consisted of 90 per cent. safrol (*q.v.*) and 10 per cent. of a terpene which he termed safrene, with traces of a phenol, which was afterwards identified as eugenol. A recent investigation in Schimmel's laboratory has shown that "safrene" is a mixture of the terpenes pinene and phellandrene; dextro-camphor was also found, and a body which

was probably cadinene. The average composition of the oil is :—

Safrol	80 per cent.
Pinene	10 ,,
Phellandrene . . .	
Dextro-camphor . .	7 ,,
Eugenol	0·5 ,,
Cadinene (?) . . .	2·5 ,,

This oil is used on an enormous scale for soap perfumery. Its strong odour and low price enable it to be used for the very cheapest of soaps, not only to give them an actual perfume, but also to cover up the bad odour of poor quality fats. But its use has been very largely diminished by the discovery that its active constituent exists in notable quantity in crude camphor oil. By means of fractional distillation and freezing (safrol melts at about 8°), this body can be extracted in a state of almost absolute purity as a water-white liquid of specific gravity over 1·100. In this form it is, in the author's opinion, preferable in every way for cheap perfumery to the natural oil of sassafras, and its manufacture is now an enormous industry. There are many samples, however, on the market of so-called "artificial sassafras oil" which are merely fractionated camphor oil, of specific gravity about 1·070. It should be remembered that these are often of low specific gravity and contain not more than 50 per cent. of safrol, and are far less valuable than the pure safrol. This body can, of course, be frozen out from ordinary sassafras oil, but it is much cheaper to obtain it from camphor oil. Safrol, which is identical with "shikimol" from oil of *Ilicium religiosum*, also finds an extensive use in the manufacture of heliotropine (piperonal), which is one of its oxidation products.

Sassafras leaves also yield a small quantity (·03 per cent.) of an essential oil, differing entirely from the oil from the wood. This has been investigated in Schimmel's laboratory.

The oil obtained from 8000 lb. of leaves was only about 2½ lb., and was of a light yellow colour and agreeable lemon odour. Its specific gravity was ·872, and its optical rotation + 6° 25′. The constituents identified were citral, pinene, phellandrene, a hydrocarbon of the paraffin series, a hydrocarbon also found in oil of bay and called by the discoverers myrcene, and the acetic and valerianic (isovalerianic ?) esters of linalol and probably of geraniol, and, possibly, cadinene. No safrol could be detected.

Camphor Oil.—Ordinary camphor oil is a by-product in the manufacture of the ordinary or "Japan" camphor. The tree yielding this is perhaps best known as *Camphora officinalis*, but it has been known under several other names, such as *Cinnamomum camphora* and *Laurus camphora*. The tree is distributed throughout the eastern provinces of Central China, on the island of Hainan, and to a very great extent in Formosa. The Japanese islands Kinshû and Shikoku also produce it very abundantly. According to Yoshida, the older trees contain more camphor than the young ones, and those over a hundred years of age are exceedingly rich. The importance of a regular supply of both camphor and camphor oil is enormous, and the utter neglect which the Chinese gatherers have shown to the cultivation of the tree is very surprising. They have largely succeeded in exterminating it along the seaboard of Formosa, and are continually making fresh inroads into the inland forests, without any serious attempt to replace the trees destroyed. The crude method of preparing camphor from the trees is as follows. The tree is felled and the young branches and twigs are chopped up and packed in perforated jars, and heated over a crude steam bath. The steam enters the jars, saturates the chips, and causes the crude camphor to sublime and condense in earthenware pots placed over the jars. The crude camphor is sent to the port, and a certain amount of oil exudes from it which

is collected and is known as oil of camphor. The majority of the oil is, however, produced by distilling the chips with water in crude stills. The crude product amounts to about 3 per cent. of the wood used. The oil is drained from the crystalline camphor, of which it retains a considerable amount in solution. This is transferred to a still, and about two-thirds is distilled off, leaving the bulk of the camphor in the residue, which is cooled and pressed to separate more camphor. This process is repeated so long as it pays, and the residue forms the camphor oil of commerce. From a scientific point of view, one must regard the whole of the products of distillation of the wood as camphor oil. This, however, contains so much solid camphor, or stearoptene, that it is commercially regarded as a separate product, and the liquid portion of the oil is thus known as oil of camphor. Hence the great variability in its properties and composition.

The crude camphor arrives in England in various states of purity, and is refined by sublimation, generally with quicklime and charcoal. For details of the process adopted the reader is referred to Pereira's *Materia Medica*, vol. ii., pt. i., p. 450, and Sawyer's *Odorographia*, pt. i., p. 339, where useful accounts are given. The camphor tree is also being successfully cultivated in Florida (see Brannt, *Animal and Vegetable Fats and Oils*, vol. ii., pp. 412, 413). Formerly camphor oil was regarded as having no value. To-day, however, it is used to an enormous extent in the preparation of safrol (see *Oil of Sassafras*). The earliest scientific investigation of this oil was by Beckett and Wright (*Journ. Chem. Soc.*, 1876, p. 7), but the only conclusions they came to were that it was a complex mixture probably containing a hydrocarbon of the terpene series, a body having the composition $C_{10}H_{18}O$, a liquid containing less hydrogen than camphor, and much ordinary camphor. Oishi (*Chem. News*, l., p. 275) described it as a crude oil, of specific gravity 959,

which yielded about 25 per cent. of camphor. The rectified oil was a colourless liquid of specific gravity ·895. He concluded that the oil was a mixture of terpenes, camphors, and some of the oxidised hydrocarbons. Yoshida (*Journ. Chem. Soc.*, 1885, p. 782) separated the oil into four chief portions, which appeared to be (1) a terpene (pinene) boiling at 150°; (2) a terpene (limonene) boiling at 172°; (3) camphor; (4) an oxygenated body which he termed camphorogenol. A sample examined by Trimble and Schroeter (*Pharm. Journ.*, xx., p. 145) was separated into ten fractions, each of which the authors claimed to be pure compounds, but which were clearly mixtures in several cases. No less than five terpenes were given, and five oxygenated bodies. Schimmel & Co. have examined the oil since, and to them is due the discovery of the presence of safrol, which they now manufacture on an enormous scale. They also showed that Yoshida's camphorogenol had no existence. The result of their researches shows that the following bodies are present in the oil: Pinene, phellandrene, camphene, dipentene, cineol, camphor, safrol, eugenol, borneol, *l*-terpineol and cadinene, with traces of carvacrol, aldehydes and acids, of which latter one of the oleic series, with the formula $C_9H_{16}O_2$, has been isolated. Fifteen years ago the camphor oil of commerce, according to Schimmel, had a specific gravity 1·100, but owing to the extraction of as much as possible before it is allowed to leave Japan, most of that found on the market to-day has a specific gravity seldom exceeding 0·990. It is dextro-rotary.

MacEwan gives ·943 and ·959 as the specific gravity of a Formosa and a Japan oil respectively, which he examined. As by-products in the manufacture, the separated constituents are sold as light and heavy camphor oil according to their specific gravity and boiling point. Samples are often found in London under the name of light camphor oil, with a specific gravity as low as ·880 and less, consisting almost

entirely of terpenes. The only use for the latter body is as a solvent for resins, or for cleaning purposes—indeed, as a partial substitute for turpentine.

The so-called black camphor oil is that portion of the oil boiling at a higher temperature than does camphor, and containing an appreciable amount of safrol. Its specific gravity varies between 0·950 and 1·000 as a rule. The high boiling fractions with much safrol and a specific gravity about 1·060 to 1·075 are sold as "artificial sassafras oil". Adulterations with turpentine are common.

These details show that camphor oil must be bought for what it is worth. No definite standards can be laid down, and only a complete analysis will show the value of a given sample.

The following figures, however, will be of assistance to the analyst. The oil is always dextro-rotary varying from + 12° in high gravity samples to + 20° to + 32° in lighter oils. Ligut camphor oil, of specific gravity 0·870 to 0·910, will usually yield the following fractions on distillation:—

175° to 180°	about 25 % to 35 %
180° to 185°	30 % to 45 %
185° to 190°	10 % to 15 %

Some oil obtained from German East Africa was found, after separation of the bulk of the camphor by filtration, to have a specific gravity 0·9236 and optical rotation + 39°. It contained traces of a phenol, probably carvacrol, but no eugenol, nor more than traces of borneol, and no safrol.

Borneo camphor, or borneol, the product of the tree *Dryobanalops camphora*, yields a corresponding oil, of specific gravity about ·900, which consists chiefly of terpenes. It is not, however, a commercial article.

The leaves of the Japan camphor tree also yield an essential oil. According to Hooper (*Pharm. Journ.* [56], vol. ii., p. 21), the yield is about 1 per cent. of an oil of specific gravity ·9322

and optical rotation + 4° 32′. It contained 10 to 15 per cent. of camphor. Another specimen contained 75 per cent., and had a specific gravity ·9314 and optical rotation + 27°. There seems not to be much difference between this and the ordinary camphor oil. The roots yield an oil of quite similar character. A sample distilled by Schimmel & Co. had a specific gravity ·975, and consisted chiefly of camphor—the liquid portion resembling commercial camphor oil very closely.

Culilaban Oil.—This is distilled from the fruit of *Cinnamomum culilavan*, which yields from 3 to 4 per cent. of the oil. According to Schimmel, the oil has a specific gravity of about 1·050. It is too dark for its optical rotation to be conveniently determined. The constituents found in the oil are eugenol, methyl-eugenol and possibly terpineol, and a small quantity of some constituent or constituents with a specific gravity lighter than that of water. It is soluble in 3 volumes of 70 per cent. alcohol.

Massoi Bark Oil.—This oil is distilled from the bark of *Massoia aromatica*, in which it occurs to the extent of 6 to 8 per cent. Woy, who investigated the oil (*Arch. Pharm.* [3], xxviii., p. 22), states that it contains a considerable quantity of eugenol, with some safrol, a body resembling creosote, and traces of free acetic acid. He also claimed that it contains a terpene not identical with any already known hydrocarbon. Wallach has, however, shown that this body is a mixture of the terpenes pinene and limonene, with, perhaps, some dipentene. The oil is a clear yellow liquid of clove-like odour of specific gravity 1·040 to 1·060.

Kuromoji Oil.—The leaves and young twigs of *Lindera sericea*, one of the Japanese *Laurineæ*, yield the oil known in commerce under this name. It is a dark yellow oil with a strong aromatic and balsamic odour, of specific gravity from ·890 to ·915, usually about ·900, and faintly laevo-rotary. It has been examined by Kwasnik, who states that it contains

dextro-limonene, dipentene, inactive terpineol and *laevo*-carvone. The oil, on account of its comparatively low price, has recently come into some favour as an aromatic.

Schimmel & Co. have examined a sample distilled by themselves and found it to contain 9·5 per cent. of esters calculated as geranyl acetate. Distilled at 4 mm. pressure, it yielded the following fractions:—

Temperature.	*Rotation.*
35° to 40°	- 22° 26′
40° to 45°	- 15° 44′
45° to 50°	- 9° 38′
55° to 65°	- 1° 56′
66° to 70°	+ 1°
70° to 78°	- 3° 56′
78° to 81°	- 12° 37′
Residues.	- 6° 10′

Linalol was detected in the oil, as well as geranyl acetate.

Paracoto Bark Oil.—The botanical origin of the tree which yields this oil is not known with certainty, but it appears to be a lauraceous plant growing chiefly in Bolivia (or, possibly, one of the *Monimiaceæ*). The yield is from 1 to 2 per cent. of an agreeably smelling oil of specific gravity from ·925 to ·950. It is slightly laevo-rotary, usually about - 3°. An elaborate account of its composition is given by Brannt (*Animal and Vegetable Fats and Oils*, vol. ii., p. 420), but it is extremely doubtful whether any one of the five constituents there mentioned—*viz.*, α-paracotene, β-paracotene, α-paracotol, β-paracotol, γ-paracotol—have any existence. The only well-ascertained constituents, according to Wallach and Reindorff, are methyl-eugenol and the sesquiterpene cadinene. For some interesting notes on the botany of the tree, see Elborne (*Year Book of Pharmacy*, 1893, p. 237).

Persea Oil.—The dried leaves of *Persea gratissima* yield about ·5 per cent. of an oil of specific gravity ·960, refractive

index 1·5160, and optical activity about + 2°. It contains, amongst other ingredients, methyl-chavicol.

A sample recently examined by Schimmel, who states that it is known in the south of France as *Essence d'Avocatier*, had a specific gravity 0·956; optical rotation + 2° 22′; refractive index 1·5139; ester value 3·8; acetyl-ester value 18·9. It was soluble in 6 volumes of 80 per cent. alcohol with slight cloudiness and separation of solid hydrocarbons.

Pichurim Oil.—The cotyledons of *Nectandra Puchury major* and *Nectandra Puchury minor*, two species of *Laurineæ* indigenous to Brazil, yield about ·5 to 1 per cent. of a yellowish-green oil. According to Müller, the oil contains several oxygenated constituents not completely identified. Esters of lauric and valerianic acids are probably present. It distils between 180° and 270° and contains a terpene and probably a little safrol. The fraction boiling at 256° has a deep blue colour.

Spice Wood Oil.—The various parts of the plant *Laurus benzoin* (*Benzoin odoriferum*), commonly known as spice wood or wild allspice, yield aromatic volatile oils. The plant is a North American shrub, inhabiting damp, shady woods in localities extending from Canada to Florida. Messrs. Schimmel & Co. (*Report*, October, 1890) state that all parts of the shrub possess pleasant aromatic odours, which, however, are very different from one another. They obtained: (1) From the bark, ·43 per cent. of an oil smelling like wintergreen. Its specific gravity was ·923, and its constituents boiled between 170° and 300°; (2) from the berries, 5 per cent. of an oil of a spicy aromatic odour, of specific gravity ·855, with constituents boiling between 160° and 270°; (3) from the twigs, ·3 per cent. of an oil smelling like camphor and calamus, specific gravity ·925; (4) from the leaves, ·3 per cent. of an oil of pleasant lavender odour, specific gravity ·888.

The oil from the bark appears to consist largely of hydro-

carbons, but also to contain about 10 per cent. of methyl salicylate. Morris Jones (*Amer. Journ. Pharm.*, 1873, p. 300) states that it contains a compound of the cinnamic series.

Californian Bay Oil.—The tree yielding this oil is a large forest tree, common on the mountains of California and the Pacific slope, known as the mountain laurel, sassafras laurel, or Californian olive. Botanically, it is *Umbellularia Californica* (*Oreodaphne Californica*, Nees). Heaney (*Amer. Journ. Pharm.*, 1875, p. 105) states that the yield of oil from the leaves is 4 per cent. He claimed to have found about 35 per cent. of a hydrocarbon and 65 per cent. of an oxygenated body, which he termed *oreodaphnol* in the oil. This body, however, has never received confirmation, and it is very doubtful whether the hydrocarbon he obtained was pure. He assigned to it a specific gravity ·894 and boiling point 175°. Stillman, on the other hand, claims that it contains terpineol and an oxygenated body of the formula $C_8H_{12}O$, which he named umbellol. According to Schimmel, the only well-ascertained constituent is cineol. The oil is a straw-coloured liquid of aromatic taste, having an optical rotation about − 22° and a specific gravity from ·930 to ·950. Power has examined this oil recently and has definitely recognised the following constituents: (1) Traces of free fatty acids including formic acid; (2) 1·7 per cent. of eugenol; (3) 6 per cent. of pinene; (4) 20 per cent. of cineol; (5) 60 per cent. of a new unsaturated cyclic ketone of a mint-like odour boiling at 220°, of specific gravity 0·858 and optical rotation − 37°. Its formula is $C_{10}H_{14}O$, and Power has named it umbellulone; (6) a small quantity of safrol; (7) 10 per cent. of eugenol methyl ether. The derivatives and constitution of umbellulone are discussed fully in the *Journal of the Chemical Society*, 1906, 1104. This oil must not be confused with the ordinary bay oil, which is the product of one of the *Myrtaceæ*.

Laurel Oil.—The leaves of the sweet bay, *Laurus nobilis*,

yield from 1 to 3 per cent. of an essential oil of specific gravity ·920 to ·930 and optical rotation – 15° to – 18°; the berries also yield an oil closely resembling that of the leaves, but under 1 per cent. is obtained. It is soluble in 3 volumes of 80 per cent. alcohol. Both oils contain the terpene pinene and cineol, with traces of eugenol and probably methyl-chavicol. Traces of free acetic, isobutyric and valeric acids are also present.

Tetranthera Oil.—The fruit of *Tetranthera citrata* yields about 5 per cent. of an aromatic oil of specific gravity usually about 0·890 to 0·900, but varying somewhat widely. Its only well-ascertained constituent is citral and a terpene.

Caparrapi Oil.—This oil is yielded by the so-called "canelo" tree of Colombia, *Nectandra caparrapi*. It varies in colour from pale yellow to dark brownish red, and is known in commerce under the name of "white" and "black". It is a thick liquid of specific gravity about ·915 to ·935, and rotary power – 3°. On exposure to prolonged cold, crystals of an acid are deposited. The black oil probably owes its colour to overheating. From a sample of the white oil, Tapia (*Bull. Soc. Chim.*, 1898, 638) has extracted an acid of the formula $C_{15}H_{26}O_3$, which crystallises in white needles, melts at 84·5°, and has a rotary power $[\alpha]_d = + 3°$. In addition to this body the oil contains a sesquiterpene alcohol, $C_{15}H_{26}O$, which the same chemist terms caparrapiol. It has a specific gravity ·9146, and a rotary power $[\alpha]_d = - 18·6°$, and boils at 260° at atmospheric pressure. By abstracting water by means of dehydrating agents, a sesquiterpene $C_{15}H_{24}$ is formed, termed caparrapene. This is described as a colourless liquid, boiling at 240° to 250°, and of specific gravity ·9019 and a rotary power $[\alpha]_d = - 2·2°$. These compounds require further examination before they can be regarded as new compounds. The oil is used for the same purposes as balsam of copaiba.

N. O. Myristiceæ.

There is only one genus of this natural order yielding essential oils that are at all well known. This is the genus *Myristica*, the fruit of which consists of the well-known nutmeg enclosed in a shell, which is covered by an arillus (according to Planchon, this latter is only an extension of the exostome, and therefore a false arillus, or arillode). The arillus is known as mace, and from both this and from the nutmeg essential oils are distilled. For a most exhaustive and thorough treatment of the nutmeg and its products, there is no work to equal that recently published in Berlin by Dr. Warburg on *The Nutmeg: its History, Botany, Cultivation, Commerce and Use*, to which the reader is referred for detailed information. For the present purpose, the following details will suffice:—

This natural order is confined to the tropics, and *Myristica fragrans* is the typical plant yielding the ordinary nutmeg. It is an inhabitant of the Moluccas, being specially abundant in the Banda Isles, three of which, Lontar, Pulo Ai and Pulo Nera, are often known as the "Nutmeg Islands". At one time the Dutch attempted to confine the cultivation to these islands, and when supplies were rather more abundant than usual the excess was said to have been burned in order to keep up prices. The seed was however conveyed elsewhere by the "nutmeg bird," who in swallowing the fruit digested the mace, but voided the nutmeg uninjured. The tree has been successfully introduced into numerous other places, for example, Java, Penang, Bourbon, Zanzibar and Singapore. A useful description of the cultivation of the tree will be found in the *Journal of the Indian Archipelago*, v., p. 78. Nutmegs are often imported limed, *i.e.*, treated externally with lime, with the object of preventing their germination and keeping them protected from insects. Although quite

unnecessary, this practice is approved of in certain markets, so much so that Penang nutmegs, the most valued in the London market, which are imported unlimed, are frequently limed in London for re-exportation. The nutmegs of other species are often used, both as nuts, mace and oil, as a substituent or adulteration of the ordinary product. Amongst these are the Malabar nutmegs (from *M. Malabarica*) and New Guinea nutmegs (from *M. Argentea*).

Nutmeg Oil.—Nutmegs yield from 8 to 15 per cent. of volatile oil on distillation. The *British Pharmacopœia*, in which this oil is official, allows to it a specific gravity ·870 to ·910, but in the author's opinion these limits should be rather wider—from ·865 to ·920. It also states that it should leave no crystalline residue on evaporation in a water bath. This is to guard against the presence of traces of the fixed or fatty oil existing in nutmegs, which is carried over mechanically during the distillation. The presence of traces of the fatty oil is said to be objectionable when the oil is used for the flavouring of *sal volatile* (aromatic spirits of ammonia). It may be detected by evaporating the oil, and purifying the crystals by washing them several times with cold alcohol and recrystallising from boiling alcohol. The resulting *myristic acid* melts at 54° to 55°. The oil should be dextro-rotary from + 14° to + 30°, and should be soluble in 3 volumes of 90 per cent., or in an equal volume of 95 per cent. alcohol. Its refractive index is about 1·4765. The chemistry of this oil requires clearing up, as there are many contradictory statements in connection with it. The earlier researches of Schacht (1862), Cloez (1864), and Koller (1865) are by no means in agreement. Gladstone (1872) claimed to have discovered a body boiling at about 212°, to which he assigned the formula $C_{10}H_{14}O$ and named myristicol. This body, however, is, as shown by Power and Salway, a mixture of alcohols. Wright (1873) states that the chief constituents were two

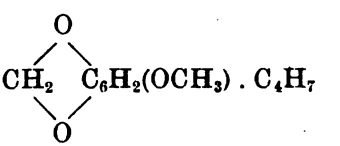
terpenes and some cymene, besides a high boiling oil of the formula $C_{10}H_{13}O_2$, and a non-volatile resin of the formula $C_{40}H_{56}O_5$. On the other hand, Semmler (*Berichte*, 1890, p. 1803) has examined the oil and states that he can find no cymene, no myristicol, and no high boiling constituent of the character above referred to. In support of these statements, he also adduces the evidence of several combustions and a molecular weight determination. His results show that the carbon and hydrogen in the oil amount to over 99·5 per cent., and the molecular weight determination (vapour-density determination) gave 138 as against a theoretical 136 for terpenes. Hence Semmler concludes that the oil consists almost entirely of terpenes. It must be noted, however, that the oil upon which Semmler worked had a specific gravity ·8611 and was not prepared by himself. Hence, although its purity appears unquestionable, it is probable that it had been rectified and the high boiling constituents got rid of, for ordinary commercial oils always possess a higher specific gravity than this. The statement occurring in Sawyer's *Odorographia*, that Semmler discovered myristicin in oil of nutmegs, is not correct. Wallach has isolated pinene from the oil and dipentene is present in traces. The oil also contains Semmler's myristicin (see *Oil of Mace*).

Much of the confusion in regard to the chemistry of this oil is due to the indifferent use of the terms oil of nutmeg and oil of mace. The most reliable investigation is that of Power and Salway (*Jour. Chem. Soc.*, 1907, 2037). The oil investigated had a specific gravity 0·8690, and a rotation of +38° 4′. These chemists have shown that the oil contains the following constituents:—

Eugenol and isoeugenol, about 0·2 per cent.
Dextro-pinene and *d*-camphene, 80 per cent.
Dipentene, 8 per cent.

d-Linalol
d-Borneol
i-Terpineol
Geraniol
} about 6 per cent.
An alcohol not yet identified.
Traces of an aldehyde resembling citral.
Safrol, about 0·6 per cent.
Myristicin, $C_{11}H_{12}O_3$, about 4 per cent.
Traces of myristic acid.
Formic, acetic, butyric and octoic acid as esters.
An acid of the formula $C_{13}H_{18}O_3$.

Mace Oil.—Much of the mace oil of commerce is merely nutmeg oil, distilled from poor quality nutmegs. The true mace oil is much more expensive, but scarcely differs from nutmeg oil. Its specific gravity varies between ·890 and ·932, and its optical rotation is about + 10° to + 20°. The yield of oil is from 4 to 15. Some of the mace of commerce has been extracted with alcohol before being imported, hence its low yield of essential oil. With regard to the chemistry of this oil, Wallach identified in it *dextro-* and *laevo*-pinene and dipentene. Semmler (*Berichte*, 1890, p. 1805) confirms the presence of about 50 per cent. of terpenes. About 15 per cent. distilled between 70° and 114° at 10 mm. pressure and appeared to contain alcohols of the formula $C_{10}H_{16}O$. The higher boiling portion contained a phenol and a crystalline compound forming white needles melting at 30°, to which the investigator assigned the formula $C_{12}H_{14}O_3$ and the name myristicin. This name is unfortunate, as it is in no way related to the glyceride of myristic acid, known under the same name and occurring in the fixed oil of nutmeg. Semmler's myristicin is, according to Thoms, chemically *oxymethylene-methoxy-allylbenzene*, of the constitution—



thus occupying a position between piperonic and apionic aldehydes. It boils at 149·5° and has a specific gravity 1·150 at 25°. Other formulæ have, however, been suggested for this body.

N. O. Euphorbiaceæ.

Cascarilla Oil.—The bark of *Croton elutheria*, a native of the Bahamas, usually known as cascarilla bark, yields from 1 to 3 per cent. of an aromatic oil. It is a light brown liquid of specific gravity ·890 to ·930, and dextro-rotary to the extent of + 5°. Its refractive index is about 1·4885. Little is known of the chemistry of the oil, but it probably contains at least one terpene and one oxygenated body. Its use is very limited in the preparation of certain perfumes and cordials. The bark itself is very aromatic, and when burned gives off sweet-smelling vapours, which accounts for its frequent employment in the manufacture of fumigating pastilles.

Thoms has isolated 2 per cent. of free acid from the oil, which is isomeric with undecylenic acid, $C_{16}H_{20}O_2$, and to which he gives the name cascarillic acid. He also finds present a little palmitic and stearic acids. A little eugenol was found and a terpene not yet identified. Cymene is present and, possibly, laevo-limonene. Two sesquiterpenes are present, boiling at 255° to 257° and 260° to 265° respectively, and an alcohol, $C_{15}H_{23}OH$, boiling at 280° to 290°.

N. O. Cupuliferæ.

The only oil of importance yielded by this natural order is that from the bark of *Betula lenta*, the sweet birch, but as this is almost identical with, and usually substituted for, that from *Gaultheria procumbens*, one of the Ericaceæ, it will be more conveniently described with the latter (*q.v.*).

N. O. SANTALACEÆ.

Santal-wood Oil.—The chief santal-wood oil of commerce, which is largely employed in medicine and perfumery, is the product of distillation of the wood of *Santalum album*. This oil is known as East Indian santal-wood oil. Probably the Macassar oil is the product of the same tree. *Santalum album* is a native of the mountainous parts of India, but is especially found in Mysore, Malabar and Coimbatore. It likewise grows on the Coromandel coast, in Madura and Assam. In the Madras presidency and Mysore it is now grown on Government plantations from seeds; experiments in this direction have been carried out in West Australia (which yields another species of santal), but hitherto without success. The wood is sold at the Government auctions, and the latest classification—for the various woods are not of equal value—with which the billets are marked is as follows:—

1. *First Class Billets* (or *Vilayat Budh*). Consists of thoroughly sound billets weighing not less than 20 lb., and not exceeding 112 pieces to the ton.
2. *Second Class Billets* (or *China Budh*). Consists of slightly inferior billets weighing not less than 10 lb., and not exceeding 224 pieces to the ton.
3. *Third Class Billets* (or *Panjam*). Consists of billets having small knots, cracks and hollows, weighing not less than 5 lb., and not exceeding 448 pieces to the ton.
4. *Chotla* (or billets of short length). Consists of short sound pieces, no limit as to weight or number.
5. *Chat Badala*. Consists of billets with knots, cracks and small hollows at either end, weighing not less than 10 lb., and not exceeding 240 pieces to the ton.
6. *Bagaradad*. Consists of solid pieces, without limit as regards dimensions, weight or number.

   N.B.—Billets of Classes 5 and 6 are not planed nor are their edges rounded off.
7. *Roots* (First Class). Consists of pieces weighing not less than 15 lb., and not exceeding 150 pieces to the ton.
8. *Roots* (Second Class). Consists of pieces weighing not less than 5 lb., and not exceeding 448 pieces to the ton.

9. *Roots* (Third Class). Consists of small and side roots below 5 lb. in weight.
10. *Jugpokal* (First Class) (or *Badala*). Consists of hollow pieces weighing not less than 7 lb., and not exceeding 320 pieces to the ton.
11. *Jugpokal* (Second Class). Consists of hollow pieces weighing not less than 3 lb.
12. *Ain Bagar*. Consists of solid, cracked and hollow pieces, weighing not less than 1 lb.
13. *Cheria* (or large *Chilta*). Consists of pieces and chips of heartwood weighing not less than ½ lb.
14. *Ain Chilta*. Consists of pieces and small chips of heartwood.
15. *Hatri Chilta*. Consists of heartwood chips and shavings obtained by planing.
16. *Milwa Chilta*. Consists of pieces and chips having in fair proportions heartwood and sapwood.
17. *Basola Bukni*. Consists of small heartwood and sapwood chips.
18. *Sawdust* (or *Powder*). Obtained in sawing the santal-wood.

The yield of oil is very variable, sometimes falling as low as 1½ per cent., sometimes rising to 6 per cent. In order to extract the oil, the wood must be rasped as fine as possible by special machinery and distilled with high pressure steam. The native distillers use an open fire, and naturally obtain a very inferior oil. The oil is largely used in medicine and perfumery, and is official in the *British Pharmacopœia*. It is a pale yellow, sometimes almost colourless, thick oil of characteristic aromatic odour, of specific gravity about ·975 to ·982 or rarely up to ·985. The 1885 *Pharmacopœia* gives the figure as ·960, but the 1898 edition has corrected this obvious error and gives ·975 to ·980. The earlier fractions of the distillation have a lower gravity than the later ones, so that unless the process be carried to its extreme limit the oil may have a rather lower gravity than that allowed by the *B. P.* This point is illustrated by the following three fractions—the first, middle and last two ounces from a 20 lb. batch of oil, distilled by the late Mr. Conroy for the author:—

First	·9649
Middle	·9758
Last	·9808

The optical rotation of the oil is fairly constant, seldom varying outside the limits − 15° to − 20° (the *B. P.* gives − 16° to − 20°). Sometimes a rotation as low as − 12° is observed, but in the author's opinion this is due to the use of old or rotten wood. An important feature in examining the oil is its solubility in from 5 to 6 volumes of 70 per cent. alcohol. Its high boiling point is also characteristic. Under ordinary pressure it undergoes slight decomposition, but at 14 mm. nothing should distil over under 150°, whilst 80 to 90 per cent. of cedar-wood oil, a common adulterant, is obtained below this temperature. The refractive index of this oil is from 1·505 to 1·510. An important method of examining the oil is the acetylation process (*q.v.*) first applied by the author to this oil (*Pharm. Jour.*, lv., p. 118). Santal-wood oil requires from ·7 to 1·5 per cent. of potassium hydroxide to saponify the esters present. After acetylation, however, the oil requires about 20 to 21 per cent. of KOH to saponify it, thus indicating the presence of a large quantity of alcoholic constituents. The details of this process, and the calculations required, have been given on page 116. The free alcohols are usually calculated as santalol $C_{15}H_{26}O$, and should never fall below 90 per cent., and in good oils rarely below 93 to 94 per cent. Cedar-wood oil, gurjun oil, and copaiba oil all yield a very low acetylation figure (calculated as santalol, as follows: cedar oil, 8 to 12 per cent.; copaiba oil, 5 to 8 per cent.; gurjun oil, 7 to 10 per cent.). Castor oil is also sometimes added as an adulterant, but is easily detected on account of its lower gravity and high saponification number.

The author has recently found numerous samples containing terpineol and also West Indian santal oil. The author and Bennett have examined the properties of a number of acetylated santal oils. A genuine oil should, on acetylation, give figures within the following limits:—

Specific gravity	= 0·985 to 0·989
Optical rotation	– 12° to – 15°
Refractive index	= 1·4890 to 1·4920

Oil drawn from Macassar wood has usually a lower specific gravity than that from Mysore wood, and a lower optical rotation and santalol value. Four samples gave the following figures :—

Specific Gravity.	*Optical Rotation.*	*Santalol.*
0·975	– 15° 24′	91 %
0·975	– 10° 36′	88 %
0·976	– 15° 48′	90 %
0·974	– 16° 6′	92 %

Chapoteaut examined this oil (*Bull. Soc. Chim.*, xxxvii., p. 303) and stated that it contained the aldehyde santalal $C_{15}H_{24}O$ and the alcohol santalol $C_{15}H_{26}O$, the former being in excess. But as the oil upon which he worked had a specific gravity ·945, his results are not reliable. The author's experience, now amply confirmed by all observers, is that the alcoholic constituent or constituents largely predominate. Chapman (*Proc. Chem. Soc.*, clxiv., p. 140) claims to have isolated santalal $C_{15}H_{24}O$ as a liquid of specific gravity ·9793 and specific rotation – 14° 42′, but no proofs of its purity are adduced. Santalol is now an article of commerce. A sample prepared by Schimmel & Co., and examined by the author, had a specific gravity ·979 and an optical rotation – 18°. The author has repeatedly expressed the opinion that "santalol" is not a pure compound, but a mixture of more than one alcohol. This opinion has recently been confirmed by Schimmel & Co., who give the following details of their examination of samples of this body (*Report*, April, 1899, p. 38).

East Indian sandal-wood oil consists of 90 to 98 per cent. of alcoholic constituents, commonly called santalol. This is obtained by saponifying the oil and by subsequently rectifying it by distillation under low pressure or with over-

heated steam. A recent comparative examination of several samples gave the following results:—

Sample.	*Specific Gravity.*	*Saponification Figure (% KOH).*	*Boiling Point 11 mm. pressure.*	*Percentage of Santalol calculated for $C_{15}H_{26}O$.*
1	·979	·13	168° to 169°	98·8
2	·980	·63	—	100·3
3	·979	·80	168° to 170°	99·3
4	·979	·35	—	100·1

As is to be seen from these figures, the saponification in no case has been complete. In order to prepare pure santalol we proceeded in the following way: 100 grammes of East Indian sandal-wood oil of specific gravity ·977 and saponification figure ·44 and containing 94·1 per cent. of santalol were heated to 80° with an equal weight each of phthalic anhydride and benzene upon a water bath for one hour; the acid esters formed were combined with alkali and dissolved in an excess of water. The aqueous solution was deprived of the non-alcoholic constituents by agitation with ether, repeated three times, and the acid esters were separated by the addition of dilute sulphuric acid; subsequently they were saponified by means of alcoholic solution of potassium hydroxide, and the santalol set free was deprived of adhering alkali and alcohol, by washing it with water. By fractionating under 13 mm. pressure the following fractions were obtained:—

1. 170° to 172°; sp. gr. ·978; opt. rot. − 15° 22′
2. 172° „ 172°; „ „ ·979; „ „ − 18° 0′
3. 172° „ 172°; „ „ ·979; „ „ − 26° 47′

None of those fractions gave a saponification figure. The product obtained amounted to 85 per cent. of the oil used. The odour slightly resembles that of sandal-wood oil. Although this product may be devoid of esters and other "non-alcoholic" constituents, it can by no means be considered a definite chemical compound, for the reason that its

optical rotation reveals too considerable differences between the three fractions.

In order to settle this point, the first fraction was further submitted to fractional distillation and a substance obtained which boiled at 165° and 167° under 13 mm. pressure, and had the specific gravity ·970 and optical rotation – 7° 20′. Treated in the same way, fraction 3 rendered a product having a considerably higher boiling point, namely, 173° under 13 mm. pressure, specific gravity ·979 and optical rotation – 32° 36′. A substance yielding upon fractionation two products so much differing cannot be considered an individual chemical compound. Santalol, therefore, is a mixture of two sesquiterpene alcohols of which the one with a lower boiling point seems to be optically inactive or possibly dextro-rotary, while the other having a higher boiling point is strongly laevo-rotary.

Schimmel prefers to use the formula $C_{15}H_{24}O$ for calculations instead of $C_{15}H_{26}O$, which would be correct for a sesquiterpene alcohol.

It is remarkable that the esters contained in East Indian sandal-wood oil have a lower boiling point (132° to 164° under 11 mm. pressure) than the sesquiterpene alcohols. To all appearances they contain other alcoholic constituents than the santal alcohols.

It may also be stated that santalylphthalic acid could not be made to crystallise, even after it had been kept at a low temperature for weeks. Santalylphthalate of silver melts at about 50°, and is difficult to be recrystallised.

The author has pointed out that the alcohols of santal-wood oil form phenylurethanes. When the oil is mixed with phenyl-isocyanate a great rise in temperature takes place and the mass solidifies. Several compounds can be separated by fractional crystallisation, but they require further investigation.

The author and Bennett have recently found that a series of oils is offered at low prices, and although the better samples, at prices very close to that of the pure oil, have so far evaded any attempt to discover the adulteration, if any, to them, in the lowest grade we have little doubt there is present the so-called West Indian sandal oil, or, probably, a fractionated oil with the more insoluble portions removed. Two oils of this type which were examined exhibit the characters as follows:—

	1	2
Specific gravity	0·976	0·9755
Optical rotation	−10°	−9° 30′
Refractive index	1·5070	1·5068
Esters (as santalyl acetate)	5·7 %	5 %
Total santalol	82·2 %	83 %
Solubility in 6 vols. 70 % alcohol	Soluble	Soluble
Specific gravity of acetylated oil	0·983	0·9846
Rotation of	−8°	−8°
Refractive index of	1·4952	1·4963

The oils were by distillation separated into ten fractions of 10 per cent. each. The characters of these fractions show that one was dealing with a body having the properties of sesquiterpene derivatives, and the odour of the first fractions suggested West Indian oil:—

1

Fraction	Sp. Gr.	Opt. Rot.	Ref. Ind.
1	0·963	− 7°	1·5040
2	0·969	− 6° 30′	1·5060
3	0·978	− 5° 30′	1·5070
4	0·976	− 5° 30′	1·5080
5	0·977	− 5° 40′	1·5082
6	0·977	− 7°	1·5085
7	0·978	− 8° 30′	1·5089
8	0·980	− 10° 25′	1·5090
9	0·984	− 14° 45′	1·5103

2

Fraction	Sp. Gr.	Opt. Rot.	Ref. Ind.
1	0·965	– 5°	1·5086
2	0·967	– 5°	1·5048
3	0·972	– 4° 30′	1·5062
4	0·975	– 4° 30′	1·5075
5	0·976	– 5° 50′	1·5079
6	0·978	– 6°	1·5083
7	0·978	– 8°	1·5080
8	0·981	– 10° 10′	1·5090
9	0·983	– 14°	1·5095

These figures should be compared with those obtained with genuine samples of sandal-wood oil. Four samples of authentic origin gave the following results:—

A

Fraction	Sp. Gr.	Opt. Rot.	Ref. Ind.
1	0·970	– 19° 30′	1·5055
2	0·970	– 17° 20′	1·5060
3	0·972	– 16°	1·5060
4	0·974	– 16°	1·5065
5	0·977	– 15° 30′	1·5068
6	0·978	– 15°	1·5068
7	0·980	– 16° 40′	1·5079
8	0·980	– 18°	1·5080
9	0·984	– 21°	1·5084

B

Fraction	Sp. Gr.	Opt. Rot.	Ref. Ind.
1	0·975	– 19°	1·5000
2	0·969	– 18°	1·5044
3	0·969	– 18°	1·5068
4	0·972	– 16°	1·5070
5	0·979	– 14°	1·5072
6	0·979	– 15° 30′	1·5080
7	0·982	– 16°	1·5080
8	0·984	– 17° 20′	1·5075
9	0·982	– 21° 30′	1·5085

C

Fraction	Sp. Gr.	Opt. Rot.	Ref. Ind.
1	—	− 21°	1·5067
2	0·970	− 17°	1·5064
3	0·970	− 15°	1·5063
4	0·974	− 15°	1·5071
5	0·977	− 15°	1·5075
6	0·978	− 15°	1·5080
7	0·978	− 15°	1·5080
8	0·979	− 17°	1·5082
9	0·980	− 20°	1·5086

D

Fraction	Sp. Gr.	Opt. Rot.	Ref. Ind.
1	0·977	− 18°	1·5078
2	0·964	− 17°	1·5038
3	0·969	− 16°	1·5051
4	0·975	− 15°	1·5068
5	0·979	− 15°	1·5072
6	0·980	− 14°	1·5078
7	0·981	− 16°	1·5083
8	0·981	− 18°	1·5083
9	0·978	− 22°	1·5086

A comparison of these figures will prove of the utmost service to the analyst.

It is obvious that a dextro-rotary oil is present in these adulterated samples, which makes the optical rotation of the fractions very much lower than is the case with normal pure oils. The divergence between the fractions in pure oil is but little, and in no case was the optical rotation below − 14°.

The examination of the first three or four fractions of 10 per cent. distilled thus shows the admixture of more than a very small amount of the adulterant, and the following standards for *Oleum Santali* in the next edition of the *Pharmacopœia* are suggested:—

Specific gravity	0·975 to 0·982
Optical rotation	−16° to −20°
Refractive index	Not below 1·5080
Santalol (total)	At least 90 per cent.
Esters as santalyl acetate . . .	4 to 6·5 per cent.
Rotation of first and second fractions of 10 per cent.	Not below −16°

It should be soluble in five volumes of 70 per cent. alcohol at 20° C.

It is undoubtedly a fact that pure oils are occasionally met with which do not comply with the requirements above set out. When old wood is employed for distillation, the oil is sometimes less soluble, and if the distillation has been pushed to the fullest extent, the rotation of the oil may be reduced. It would be very unwise to enlarge the official limits so as to include these oils, as this would open a floodgate to adulteration.

Von Soden and Müller found in santal-wood oil a sesquiterpene of specific gravity 0·898 and optical rotation − 21°, boiling at 261° to 262°, and an acid melting at 154°. Guerbet has since investigated the oil and identified the following compounds (*Comptes rendus*, 1900, 417):—

1. Two sesquiterpenes $C_{15}H_{24}$, *viz.*, α-santalene (b. p. 253°, sp. gr. 0·913 at 0°, optical rotation $\alpha_d = -13{\cdot}98°$) and β-santalene (b. p. 263°, sp. gr. 0·9139 at 0°, optical rotation $\alpha = -28{\cdot}55°$); the latter is identical with the hydrocarbon formerly discovered by Von Soden and Müller.

2. A mixture of two alcohols $C_{15}H_{26}O$, of different rotatory power, which the author calls α- and β-santalol. The author has previously called attention to the fact that the so-called santalol is not a homogeneous body.

3. An aldehyde $C_{15}H_{24}O$, santalal, a body of which the existence in sandal-wood oil had already been assumed by Chapoteaut. It boils at 180° under 40 mm. pressure, and has a strong, pungent, pepper-like odour. Its semicarbazone crystallises in small needles and melts at 212°.

4. An acid $C_{15}H_{24}O_2$, santalic acid, a thick, colourless liquid, boiling between 210° to 212° at 20 mm. pressure and possessing only very weak acid properties. Its sodium and potassium salts form indistinctly crystalline masses, while the barium salt is recovered in fine needles from dilute alcohol. Santalic acid is also formed when santalal is oxidised with chromic acid in acetic acid solution.

5. An acid $C_{10}H_{14}O_2$, teresantalic acid, which crystallises out from alcohol in thick prisms and melts at 157°. This is probably identical with the acid, of a melting point of about 154°, discovered by Von Soden and Müller. It boils at 183° under 28 mm. pressure. The potassium salt forms crystalline masses with a lustre like mother-of-pearl. The calcium salt has the formula $(C_{10}H_{13}O_2)_2Ca + 2H_2O$.

6. The most volatile portions of sandal-wood oil contain minute quantities (0·2 to 0·3 per mille) of highly odorous bodies, as yet undefined. They are the chief odoriferous constituents of the oil.

a-santalene gives a nitrosochloride melting at 122° and a piperidide melting at 109°. *β*-santalene yields two nitrosochlorides melting at 152° and 106° respectively. The mixture of alcohols has been separated by Guerbet into—

(*α*) *a*-santalol, boiling at 300° to 301° at 760 mm., or at 162° to 163° at 13 mm.; of specific gravity 0·9854 at 0° and optical rotation – 1° 20′.

(*b*) *β*-santalol, boiling at 170° to 171° at 14 mm., or 309° to 310° at 760 mm.; of specific gravity 0·9869 at 0° and optical rotation – 56°.

a-santalyl acetate boils at 308° to 310°. *β*-santalyl acetate boils at 316° to 317°. Phosphorus pentoxide dehydrates these alcohols with the formation of isosantalenes:—

a-isosantalene boils at 256°; rotation = + 0° 12′.

β-isosantalene ,, ,, 260°; ,, = + 6° 6′.

To emphasise the difficulty in obtaining these isomeric

alcohols of high boiling point in a state of purity, attention must be drawn to Von Soden's later work, who gives the following figures:—

α-santalol is slightly dextro-rotary (+ 1° 40′ to + 2° 4′) and boils at 8 mm. pressure at 155°, at 752 mm. at 301° to 302°. Elementary analysis pointed to the formula $C_{15}H_{24}O$, with which the results obtained in the saponification of pure santalyl acetate agree.

α-santalylacetate boils at 311° to 312°, and at 15° has a specific gravity of 0·988. α_d = about + 3°.

The non-alcoholic constituents of sandal-wood oil have also recently been examined by F. Müller, who has isolated several new bodies.

Santene, a hydrocarbon not previously known, boils at 139° to 140°, and has a specific gravity at 15° of 0·8710. Analyses of this body and of its derivatives led to the formula C_9H_{14} by which it is suggested that this hydrocarbon represents a lower homologue of the terpenes.

Its nitrosochloride occurs in two modifications. Santene-*α*-nitrosochloride is blue, melts at 108°, and even after a short time turns into the white *β*-modification. If the latter is heated to 90°, it becomes intensely blue, changing back into the modification melting at 108°.

Santene hydrochloride is formed by passing dry hydrochloric acid into the ethereal solution of the hydrocarbon; it melts at 80°, and does not keep well on exposure to the air.

Santene tribromide is produced by adding 2 molecules of bromine to a dry chloroform solution of santene. Its melting point is 62° to 63°; it is suitable for the identification of the hydrocarbon.

Semmler (*Berichte*, 1907, 3321) gives the following as the character of the sesquiterpenes of santal-wood oil: *α*-santalene boils at 118° to 119° at 9 mm., has a specific gravity 0·8984 at 20°, refractive index 1·4910 and optical rotation − 15°.

β-santalene boils at 125° to 127°, at 9 mm., has a specific gravity 0·892 at 20°, refractive index 1·4932, and optical rotation − 35°.

Semmler and Bode (*Berichte*, 1907, 1124) have shown that santalol is a primary alcohol (or alcohols) by its oxidation to santal aldehyde. According to these chemists this aldehyde boils at 152° to 155° at 10 mm., has a specific gravity 0·995 at 20°, refractive index 1·51066 and is dextrorotary. Its semicarbazone melts at 230°.

Santalyl chloride, obtained by the action of phosphorus pentachloride on the alcohol, has a specific gravity 1·0398. Its formula is $C_{15}H_{23}Cl$ according to Semmler, who regards santalol as $C_{15}H_{24}O$.

Semmler regards santalol as a tri-cyclic compound, which, when heated to 160° with alcoholic potash for two hours, is ruptured at the double bond in the side chain and the tri-cyclic compound is converted into a di-cyclic alcohol which he calls di-cycloeksantalol. The formulæ for the two compounds which he suggests are as follows:—

$CH:CH.CH_2.CH_2.CH_2.OH$

Tri-cyclosantalol.

$CH:CH.CH_2.CH_2.CH_2.OH$

These abstruse points are dealt with fully in the following papers—*Berichte*, 1907, 40, 1120, and 1907, 40, 1124.

The portion of the first fraction of santal-wood oil boiling at 80° to 100°, at 15 mm. pressure, when treated with semicarbazide, gave a mixture of two compounds whose melting points were 175° and 224° respectively.

The semicarbazone melting at 175°, when decomposed with sulphuric acid, produced a ketone whose odour reminded

of camphor and thujone, of the formula $C_{11}H_{16}O$, which is called "santalone". It boils at 214° to 215° (at 15 mm. pressure at 88° to 89°); its specific gravity is 0·9906 at 15°, optical rotation $\alpha_d = -62°$. It forms an oxime melting at 74·5° to 75·5°.

The ketone corresponding to the semicarbazone melting at 224° has not yet been examined.

As regards the other acids contained in sandal-wood oil, which principally occur as esters, there appears to be present, besides the santalic acid $C_{15}H_{24}O_2$ of Guerbet, at least a third acid, the nature of which is still to be investigated.

Chapman and Burgess have further examined santalenic acid, obtained by oxidising "santalol" with permanganate of potassium. They assign to it the formula $C_{13}H_{20}O_2$. It melts at 76°, distils at 189° at 28 mm., and has an optical rotation + 18°.

West Australian santal-wood oil is the product of another species of santal, being chiefly if not entirely derived from the wood of *Santalum cygnorum*. Several other species are found in West Australia, but they are much less common than *Santalum cygnorum*, which alone is used to any extent for distilling. Although only a tree of small dimensions, it forms an important factor in the timber industry of Western Australia. The species, as the author has seen it growing in the interior of this colony, has a low depressed habit, and is usually very branchy and heavily topped. It is generally from 12 to 20 feet high, and from 6 to 10 inches in diameter. The stems usually weigh from 1 to 6 cwt. It is found fairly well distributed in the interior of the colony, except in the extreme south-west. It may be seen growing fairly freely on the most barren sandy soil, where one could not see a blade of grass nor a drop of water for miles round. The greater part of this wood is exported to China, but one or two santal oil distilleries have been started in the colony. The author has examined four samples of oil distilled from either *Santalum cygnorum*,

or from this tree with other species mixed (for there are several closely allied species growing in Western Australia), for which he is indebted to the kindness of Mr. Samuel Lambert, and found they had the following characteristics :—

	Specific Gravity.	*KOH for Esters.*	*Iodine Absorption.*
1	·9650	1·46	200·0
2	·9644	1·15	204·5
3	·9632	1·66	198·2
4	·9643	1·35	197·6

There was found only about 75 per cent. of alcohols in these oils, as against 90 per cent. in the East Indian oil. The distillation water of this oil contains traces of methyl alcohol, diacetyl and furfurol.

In South Australia *Santalum preissianum* is used for distillation, but it yields an oil quite different to the ordinary santal-wood oil. It has a specific gravity of about 1·02, and becomes solid when cooled.

Berkenheim has isolated from this oil a solid alcoholic constituent of the formula $C_{15}H_{24}O$, melting at 101° to 102°, and yielding crystalline esters (*Journ. Chem. Soc.*, 1893, ii., 666).

The so-called West Indian santal-wood oil is the product of a Venezuelan tree which has been identified as belonging to the N. O. Rutaceæ, but as the oil is allied so closely to the true santal-wood oils, it may be conveniently described here. Its specific gravity is lower than that of the true santal oil, and it is far more insoluble in alcohol. It is *dextro*-rotary and contains much less alcoholic constituents than does the oil of *Santalum album*. Five samples gave the following figures :—

	Specific Gravity.	*Solubility in 70 per cent. Alcohol.*	*Rotation.*	*Alcohols as Santalol.*
				Per cent.
1	·962	1 in 80	—	42
2	·966	1 in 55	+25° 30′	50·5
3	·958	Insoluble in 80	+8°	30·1
4	·963	Insoluble in 80	+30° 20′	32·1
5	·962	Insoluble in 80	+25° 75′	—

Mr. E. M. Holmes has recently examined the plant yielding this oil, and named it *Schimmelia oleifera* after the well-known Leipzig firm who obtained the specimens for him, but Urban has now proved definitely that the plant belongs to the genus *Amyris*, and has identified it as *Amyris balsamifera*.

African santal-wood oil is the product of a tree of unknown origin. The oil has a specific gravity of about ·965. It appears to resemble West Indian oil somewhat, but requires further examination. Fiji santal-wood oil is the product of the wood of *Santalum Yasi*. Umney obtained 6¼ per cent. of oil from this wood, with a specific gravity, according to MacEwan, ·9768. It is laevo-rotary – 25° 50′.

It is now well recognised that the alcoholic body or bodies of West Indian santal oil differ from the alcohols of the East Indian oil.

This alcohol has now been isolated by H. von Soden and named by him "amyrol". It forms an almost colourless, viscous liquid, which forms a clear solution with 3 to 3½ parts of 70 per cent. alcohol. Specific gravity at 15° = 0·980 to 0·982; α_d = + 27°. Boiling point at 748 mm. pressure = 299° to 301°, at 11 mm. 151° to 152°.

Amyrol cannot be esterified with phthalic acid anhydride; quantitative acetylation is equally impossible. Amyrol is probably a sesquiterpene alcohol $C_{15}H_{26}O$. In addition to this body, West Indian sandal-wood oil contains a sesquiterpene, whose nature has been investigated by E. Deussen. He introduced hydrochloric acid gas up to saturation into the oil dissolved in dry ether, and obtained crystals of cadinene dihydrochloride. The corresponding compounds of hydrogen bromide and iodide, of which the constants are given below, were produced in a similar manner.

	Melting Point.	Per cent.			$[\alpha]_D$.
		Cl.	Br.	I.	
Dihydrochloride . .	117° to 118°	25·65	—	—	− 36·65°
Dihydrobromide . .	124° „ 125°	—	43·64	—	− 36·26°
Dihydroiodide . .	105° „ 106°	—	—	54·96	—

It has more recently been found that amyrol, like santalol, is not a uniform body, but that by frequently repeated fractional distillation it can be separated into different alcohols. The higher boiling, very viscous compound has a faint, characteristic, fragrant odour; its formula is $C_{15}H_{25}OH$. Specific gravity about 0·987, α_d = about + 36°; boiling point 299°. The lower boiling alcohol appears to have the formula $C_{15}H_{23}OH$, and to be optically inactive.

The liquid obtained in saponifying the original oil, when acidified with sulphuric acid, yielded an oil, partly congealing in crystalline form, with an odour strongly reminding of acetic acid. This oil was shaken with carbonate of sodium solution to remove the acid. The remaining crystals, after recrystallisation from methyl alcohol, melted at 117°. This new body, to which the name amyrolin was given, contains neither nitrogen nor methoxyl groups; its composition is $C_{14}H_{12}O_3$. Amyrolin dissolves in alcoholic potash solution with a yellowish-green fluorescence, absorbs bromine, and yields with the latter an amorphous, white dibromide of the melting point 157° to 159°. In view of its behaviour amyrolin appears to be a lactone-like body of the aromatic series.

N. O. Aristolochieæ.

The oils produced by this family of plants are not of much importance, and are but few in number so far as is at present known.

Asarum Oil.—The ordinary European snake-wood oil is distilled from the root of *Asarum europaeum*, which yields about 1 per cent. of a thick, dark brown oil of sweet aromatic odour. The specific gravity of this oil varies from 1·015 to 1·07. According to Petersen, when frozen it deposits crystals of asarol. It also contains pinene and methyl-eugenol, or possibly methyl-*iso*-eugenol. The whole plant has been subjected to distillation by Zeller, who obtained about ·2 per cent. of an oil which is stated not to contain asarol at all.

Canadian Snake-root Oil is the corresponding product from the root of *Asarum canadense*. The yield is from 3 to 5 per cent. of an oil of strong aromatic odour, specific gravity ·930 to ·960. According to Power, this oil contains a terpene, which he called asarene, but which is now recognised as pinene, asarol, dextro-linalol, laevo-borneol, laevo-terpineol, geraniol, eugenol methyl ether, a phenol $C_9H_{12}O_2$, a lactone $C_{14}H_{20}O$, palmitic acid, acetic acids and some unidentified constituents.

Virginian Snake-root Oil is the product of distillation of the whole herb *Aristolochia serpentaria*. It is an oil of specific gravity about ·990, and, according to Schimmel, contains borneol. It possesses an odour recalling valerian and camphor. The root of *Aristolochia clematitis* also yields an oil of specific gravity about ·905, but its composition is not well known.

(B) *Gamopetalæ.*

N. O. Labiatæ.

Few natural orders yield so many essential oils of great commercial value as does this. Amongst the more important of these are lavender, peppermint, rosemary, patchouli, pennyroyal, spike and thyme oils. Several of these are amongst the best illustrations of the great effects of climate and soil on the essential oils of the same plant grown under different conditions.

Lavender Oil.—This oil is obtained by distilling the flowers of *Lavandula vera*, the well-known lavender, a native of Southern Europe. The plant is found on the stony declivities of the Provençal Alps, the lower Alps of Dauphiné and Cevennes (and even so far north as latitude 46°), in Piedmont, Switzerland, the mountains of Liguria and Etruria, and various other places. Peculiarly enough, the plants come to their greatest perfection and yield a much finer essential oil when transferred from their native soil, and carefully cultivated in certain districts in England, which produces the finest lavender oil in the world. The principal lavender plantations in England are in the neighbourhoods of Mitcham, Ampthill, Hitchin and Canterbury.

Attempts have been made to establish plantations in Southern France from young plants taken from parent stems in England; but the plants quickly reverted to their original condition, and "English" lavender oil can so far only be produced in England. For the details of the methods of cultivation adopted, the reader is referred to the excellent monograph in Sawyer's *Odorographia*, vol. i., p. 361. A great deal of the finest lavender oil is distilled with water over an open fire, and, so long as care is taken that the plants themselves are not burnt, the fine quality of the resulting oil largely justifies the process. In England it is usual to allow the body of the still in which the flowers are distilled to be very shallow as compared with its width, in order to allow the oil to pass over rapidly and get away from the source of heat, which might damage its odour. If a naked fire be used, it is customary to suspend the charge of flowers in a basket of sheet copper, with perforations all over it to allow the free circulation of water. This basket, of course, holds a large charge, and is manipulated by means of a pulley or swing-crane. The basket should be about an inch from the bottom and sides of the

still, and have copper legs to rest upon. Sufficient water is used with each charge to cover the top of the basket. The finest portion of the oil condenses during the first half-hour to hour of the distillation, and is usually reserved, the remainder being collected separately. Rectification of lavender oil, which renders it colourless, does not improve it. The somewhat "herby" odour of the fresh oil soon passes off, and if the oil be kept in cool dark places it improves by maturing for several years, and matured oils are often sold according to the date of their preparation. After a certain time it is said to deteriorate unless a little alcohol is added to it.

This oil, in common with several others distilled from plants of the natural order *Labiatæ*, is one of those whose characters are altered to a very remarkable degree by changes in the conditions of growth. An expert now will usually distinguish a lavender oil distilled from plants in and around Mitcham from one distilled in Cambridgeshire or Hertfordshire, and although the ester value of all English oils is fairly constant, foreign distilled oils invariably have much higher ester values. This difference in ester value is brought about by entirely different conditions from those which bring about a reduction in esters where the plants yielding the oil "*s'aspiquent*". There (see p. 265) it is a case of cross fertilisation of the two species of lavender.

The chief difference between English and French oils of lavender lies in the fact that the former only contains about 7 to 10 per cent. of esters calculated as linalyl acetate, whereas the latter contains up to 40 per cent. and over. Messrs. Schimmel have actively endeavoured to establish this ester content as the basis of the valuation of the oil. They maintain the superiority of fine French oil over English oil, and go so far as to say that the latter cannot compete with the former. The author, in common with most others, holds the opposite

opinion, and considers that no comparison can be made between the two oils on the basis of their ester content. This is much accentuated, if such were necessary, by the fact that linalyl acetate is not *the* odoriferous ingredient of oil of lavender. It is so much modified by the presence of other bodies, as to be regarded as only one of the odoriferous compounds in the oils. Pure linalyl acetate has a marked bergamot odour, and may be regarded as the characteristic ingredient of that oil. The fact that English oil fetches a very much higher price than French oil speaks for itself. For a comparison of oils grown in the same locality, the ester comparison may, however, be of service. The oils produced in the south of Europe are finer according as the plants are growing at greater elevations, and according to Schimmel & Co. the very finest oils are produced from the higher valleys of the Savoy Alps, yielding 44 per cent. of ester. The fine oils yielding 38 to 40 per cent. of ester are usually obtained from the Alpes Maritimes and the Basses Alpes, close to the Italian frontier. Less fine, but still excellent, oils with 28 to 32 per cent. of ester are obtained from the French departments of the Gard, Drôme and Hérault.

These statements, however, are only based on a comparison of the ester values, and are in direct opposition to the views and experience of several of the leading distillers of this oil. Lautier, for example, says (*Études sur quelques procédés et products de parfumerie*): "No one can deny that the oils from Drôme or Vaucluse are of far inferior odour to those from the Alps. Yet the former contain 35 to 40 per cent. of esters." It is also true that some of the oil distilled on the Italian frontiers with 25 to 30 per cent. of esters is of the finest grade, and Umney, who in the main agrees with Schimmel on this question, admits that with an ester value of much over 40 per cent. the oil may be rank. The "ester theory" has induced

much adulteration into artificial esters, such as ethyl succinate and citrate.

A very important contribution to the question of the ester theory is that contained in a paper by Birckenstock, and so that it may be judged fairly the following commentary on it, taken from Schimmel & Co.'s *Report* (October, 1906), is reproduced *verbatim*:—

"In a work on the influence which the cross-fertilisation of lavender and spike has on the essential oil of these plants, A. Birckenstock also deals with the ester question. Although he places himself on the standpoint likewise occupied by us, that the ester content is highly important for the valuation of lavender oil, and that the classification of the various qualities according to their content of linalyl acetate as a rule applies, he has observed that there are also good lavender oils which contain only 20 to 30 per cent. ester. Such oils are found in the Alps near the Franco-Italian frontier, and the annual production (about 5000 kilos) is in Birckenstock's opinion of sufficient importance to take the particular properties of these oils into account. They have a very fine bouquet, but no 'body'. The content of linalol amounts to about 50 per cent., and is therefore normal, but, as already mentioned, the ester content is only 20 to 30 per cent.; they are also characterised by a low specific gravity (0·878 to 0·882), and by a considerable laevo-rotation (− 8° to − 9°); they are, moreover, very readily soluble in alcohol (in 10 to 12 volumes 60 per cent. alcohol).

"A further exception to the rule, according to Birckenstock, is made by the varieties standing between lavender and spike. If, namely, lavender comes below 2300 to 2600 feet, it crosses with spike, 'elle s'aspique'; the hybrids thus formed are known among distillers by the names of '*lavandin*' or '*spigoure*,' and they represent every possible transition between lavender and spike, according to the conditions due to

altitude and state of the soil. In this connection Birckenstock's statements on the morphological differences between lavender and spike are also interesting; lavender has a non-ramified stalk, which is rarely longer than 16 inches; the blossoms are blue-violet, and have thin, heart-shaped, pointed sepals which are shorter than the bluish calyx.

"The spike plant is larger than the lavender. The stalks frequently have several ramifications, and grow to a height of up to 32 and 36 inches. The sepals are linear and of the same length as the calyx, which in this case is not bluish, but whitish.

"The influence of cross-fertilisation also shows itself in the properties of the essential oils, which behave entirely like mixtures of lavender oil and spike oil. Birckenstock has in the course of his observations examined a whole series of oils, from typical lavender oil to typical spike oil. He then found at the same time that towards lavender oil not only the ester content and alcohol content increase, but that also a gradual change takes place in the proportion of borneol to linalool and geraniol; whereas in spike oil borneol predominates, it diminishes towards lavender oil more and more as compared with linalool and geraniol. We give here still the properties of two characteristic lavandin oils:—

"1. $d_{15°}$ 0·9027; a_d – 0° 43′; ester content, 6·23 per cent.; alcohol content ($C_{10}H_{18}O$), 34·8 per cent.; soluble in 3 volumes 65 per cent. alcohol.

"2. $d_{15°}$ 0·8995; a_d – 1° 35′; ester content, 9·12 per cent.; alcohol content, 36·5 per cent.; soluble in 3 volumes 65 per cent. alcohol.

"We have here briefly reproduced Birckenstock's statements, owing to the special interest which this subject, hitherto not mentioned by us, possesses. Yet lavandin oil does not form an exception to the ester theory, formulated for lavender oil, as it is no longer the oil of the actual lavender plant, but

of a hybrid, and (as Birckenstock justly remarks) it is a matter of no concern to the trade whether it is a question of a lavender oil adulterated with spike oil, or of an oil which may be pure, but yet behaves exactly like the above-named mixture."

Lavender oil is a pale yellow oil of specific gravity ·885 to ·900, and optical rotation − 3° to − 10°. The *British Pharmacopœia* requires the specific gravity to be at least ·885, and the oil to be soluble in 3 volumes of 70 per cent. alcohol. Umney has shown that occasionally genuine English oils have a specific gravity slightly below this figure. The refractive index is about 1·4620 to 1·4675. With regard to any further tests to be applied to the oil, the place of origin must be taken into consideration. An English oil will not give an ester number outside the limits 7 to 10 per cent., calculated as linalyl acetate, whilst foreign oils yield about 25 to 44 per cent. This fact is exceedingly important in discriminating between English and mixed lavender oils. The usual adulterants of lavender oil used to be spike oil and turpentine. Neither of these oils contains appreciable quantities of ester, so that the ester determination affords much information here. Spike oil being usually dextro-rotary causes a diminution in the rotary power of the oil. American turpentine has the same effect, whereas French turpentine increases the laevo-rotation. Mixtures of spike oil and French lavender oil can be made having the same ester content as English oil, but the optical rotation is interfered with (the specific gravity is slightly raised also, but not necessarily above the limits for normal oil). To-day, however, the most dangerous adulterant one has to guard against is spike oil enriched with artificial esters.

The esters used are, in general, ethyl succinate or ethyl citrate, each of which yields a saponification value indicating a much greater amount of linalyl acetate. The specific gravity

of the oil is raised by these additions. Schimmel gives the following method of detecting ethyl succinate. About 2 grammes of the oil are saponified and the insoluble oil washed away with ether; the aqueous solution is neutralised with hydrochloric acid and diluted to 50 c.c. Ten c.c. of cold saturated solution of barium chloride are added and the liquid warmed on the water bath for two hours and then cooled. The formation of any crystalline precipitate indicates adulteration, since the barium salts of acetic and butyric acids (which are present as natural esters) are soluble. This test applies to most of these artificial esters, such as ethyl oxalate, etc.

But more recently Schimmel has found that the following method is more reliable than the use of barium salts: 10 grammes of the oil to be examined are saponified on the water bath for one hour with alcoholic potash, the contents of the flask then placed in a porcelain dish, and the bulk of the alcohol evaporated. After this the liquid is washed in a separating funnel with about 100 c.c. water, the oily portions removed by extraction with ether, the aqueous solution returned to the porcelain dish, and the bulk evaporated on the water bath. When the alkaline solution is cooled down, it is acidified with sulphuric acid, and the organic acids thus liberated absorbed with ether. The ethereal solution is placed in a dish and the ether evaporated. For the purpose of removing volatile acids (acetic acid) the residue is still heated for some time on the water bath, then cooled, and digested with ether. In this manner a fine crystalline residue remains behind undissolved. On recrystallisation from a small quantity of alcohol, white crystals are obtained, and the melting point can be determined. On fractional distillation the artificial esters will be found in the residues left after distilling off the more volatile portion and will be found to have a very high specific gravity and low refractive index. A comparison

with similar fractions of a normal oil will at once reveal the characteristic differences.

The effects of some of the common adulterants on the characters of the oil are as follows:—

Turpentine oil lowers specific gravity and solubility; further, the rotation is affected, the laevo-rotatory French turpentine oil (a_d – 20° to – 40°) raising, and the dextro-rotatory American oil (a_d up to + 15°) lowering it.

Spike oil increases the specific gravity and lowers the rotation; the solubility remains the same.

Spanish lavender oil behaves like spike oil, but has a less marked influence on the rotation.

Rosemary oil also causes similar alterations as spike oil, but renders the lavender oil less soluble.

All the additions mentioned above considerably reduce the ester content.

Lavender oil is practically neutral. An acid value over about 3 indicates the addition of acids, such as benzoic or salicylic added to bring up the apparent ester value.

Semmler and Tiemann (*Berichte*, xxv., p. 1180) showed that lavender oil contained traces of the terpene limonene, a sesquiterpene, and an alcohol together with its acetic ester, which they called lavendol. Bertram and Walbaum showed that this alcohol was in reality linalol. Schimmel & Co. detected traces of pinene and of geraniol, the latter probably existing in the form of esters. Hirschsohn has also detected traces of cineol. The chief differences between English oil and French oil are the variations in ester percentage already referred to, and in the fact that English oil contains some quantity of cineol, whereas French oil contains it only in traces (spike oil is also rich in cineol). Duyk states that borneol and its esters occur in the oil, and Bouchardat has found traces of *dextro*-camphene. Traces of a stearoptene are also found. The esters are those of acetic, butyric and

valerianic acid, and traces of coumaric are also present. A recent investigation by Schimmel has added considerably to our knowledge of this oil. Traces of valeric aldehyde and of iso-amyl alcohol were detected, and the presence of dextro-borneol confirmed. Esters of geraniol are present in small quantities, principally as acetate and caproate. Traces of furfurol were also found. A small quantity of ethyl amyl ketone, $C_8H_{16}O$, was also isolated. As a favourite perfume lavender oil is second to very few, enormous quantities of the oil being consumed in the popular form of lavender water, and it is in such diluted forms that the delicacy of the odour of the finer oils is so pronounced.

Several other species of lavender yield oils that have been superficially examined (in addition to spike oil—which is the product of *Lavandula spica*). The oil from *Lavandula pedunculata* has a specific gravity ·939 and optical rotation − 45°. It contains nearly 40 per cent. of esters, in addition to cineol and possibly thujone. The oil of *Lavandula Stœchas* (the "holy rosemary" of the Spaniards) resembles rosemary rather than lavender in its odour. Its specific gravity is about ·940. The oil of *Lavandula dentata*, of specific gravity ·926, also resembles rosemary, with a marked camphoraceous odour. Charabot (*Bull. Soc. Chim.*, xvii., p. 378) records the examination of a sample of Spanish lavender oil, but does not state its source. He found it in much free linalol, but only 3 per cent. of esters. Borneol was also present.

Spike Oil.—Spike oil, or spike lavender oil, is distilled from the flowering herb *Lavandula spica*, which grows in the same localities as *Lavandula vera*. The yield is from ·5 to 1 per cent. of an oil of much less agreeable odour than that of the true lavender, combining that of the latter plant with that of rosemary.

Pure spike oil is pale yellow to nearly colourless and

possesses a specific gravity varying from ·905 to ·920. It is usually dextro-rotary from + 1° to + 4° and occasionally up to + 7°. Its refractive index is about 1·4660. It should dissolve in three times its volume of 70 per cent. alcohol, an important test, as very small quantities of the favourite adulterant, turpentine, interfere with its solubility. Most samples are soluble in 3 volumes of 65 per cent. alcohol also, and those not answering this test should be very carefully examined. As spike oil contains a large proportion of free alcohols, it is important to estimate these. Calculated as linalol $C_{10}H_{18}O$, a pure spike oil should yield from 30 to 40 per cent. of alcohols when estimated by the acetylation process. Some Spanish oils, probably distilled from a mixture of *Lavandula* species, contain only from 20 to 25 per cent. Strictly speaking, these are not normal spike oils. Messrs. Schimmel & Co. propose distilling the first 10 per cent. from the oil and examining its rotary power. Four authentic samples gave the following results:—

Sp. Gravity.	*Rotation of Oil.*	*Rotation of first 10 per cent.*
·916	+ 7° 7′	+ 7° 11′
·915	+ 7° 3′	+ 5° 10′
·914	+ 5°	+ 7° 11′
·918	+ 5° 30′	+ 6° 7′

Adulteration with French turpentine oil to any extent would cause this fraction to be laevo-rotary. In order to ensure uniform results a Ladenburg flask is employed, as illustrated. The lower bulb should hold about 125 c.c., and 5 c.c. should be distilled from 50 c.c. of the oil.

In addition to the specific gravity, rotation, rotation of the first 10 per cent. distilled, and estimation of free alcohols, the saponification test should also be applied. Pure spike oil requires practically no potash for saponification, as it is nearly free from esters, in contradistinction to true lavender oil.

The author and Bennett have shown that (as is sometimes the case with Spanish oils) pure spike oil may be slightly laevo-rotary up to − 3°, and also yield a laevo-rotary fraction on distillation as above. The following classification of spike oils grown in different districts by Birckenstock (see under *Lavender Oil*) confirms this statement. So that the statement that pure oils are always dextro-rotary is incorrect.

Birckenstock distinguishes the following groups: Ardèche,

FIG. 16.

Hérault, Drôme, Gard, Basses-Alpes, Alpes-Maritimes and Var. Whilst according to the author, the first-named group represents the spike type proper, and yields oils of the following properties: $d_{15°}$ 0·918 to 0·921; α_d + 7° 48′ to 9° 36′; α_d of the first 10 per cent. of the distillate + 8° to + 10°; ester content, 4 to 5 per cent.; alcohol content, 21 per cent.; soluble in 3 volumes 67 per cent. alcohol,—the "Var" group somewhat approaches the lavender type: $d_{15°}$ 0·9035 to 0·905; α_d − 1° 10′

to ± 0°; a_d of the first 10 per cent. of the distillate + 2°; ester content, 2 to 3 per cent.; alcohol content, 20 to 32 per cent.; soluble in 5 to 6 volumes 60 per cent. alcohol. The other groups represent intermediate stages. Specific gravity and rotation therefore become less, whilst alcohol content and solubility increase; inasmuch as the borneol greatly preponderating in the "Ardèche" type is gradually substituted towards the "Var" type by linalool and geraniol. The laevo-rotation of the last-mentioned oil is also remarkable, but Birckenstock considers that up to − 1° 10′ this is still normal, provided that the first 10 per cent. of the distillate rotate to the right.

Our knowledge of the chemistry of this oil is chiefly due to Bouchardat, who in 1888 showed that it contained pinene and cineol (eucalyptol). Later, he proved the presence of camphor, linalol, borneol and camphene. Terpineol and geraniol are also present in small quantities. Probably a sesquiterpene also exists in this oil, but its presence has not yet been definitely proved. The similarity of the odour of this oil to true lavender and rosemary is easily explained when one considers that the chief ingredients of the oil are cineol, borneol, linalol and camphor. Linalol is an important ingredient of lavender oil, whereas cineol, borneol and camphor oil are all present in rosemary oil.

Spike oil is largely adulterated with turpentine, and probably, according to Umney, with the commoner varieties of rosemary oil. The former is detected by the alteration in specific gravity and solubility, whilst the latter interferes with the solubility and the percentage of free alcohols present. Spike oil is largely used in cheap perfumery and in the manufacture of certain kinds of lacquer for fine china manufacture. It is also largely employed as an adulterant of ordinary oil of lavender.

Oil of Rosemary.—This oil is distilled from the flowering

tops of the plant *Rosmarinus officinalis*, a native of the south of Europe. The rosemary is a plant largely influenced, as are most of the plants of this natural order, by variations in soil and climate, and the marked differences in English and foreign oils is more than can be explained by care in the method of production. The plant is grown in a few places in England, but the greater part of the commercial oil is produced in the south of Europe. Several countries on the Mediterranean littoral produce small quantities, but after the south of France the chief source of the oil is the Dalmatian islands. Spain now produces a quantity of this oil. The Dalmatian produce is chiefly brought into commerce *vid* Trieste, and this is the oil usually known in trade as Italian rosemary oil. The English oil is by far the most valued, and commands an infinitely higher price than the foreign oil. The Italian (Dalmatian) oil is the least valuable. In England and the south of France, rosemary is distilled as quickly as possible after it is cut, and in the same manner as lavender flowers. Care is taken to exclude the woody parts of the plant, as not only do these take up unnecessary room in the stills, but also yield a less valuable oil. The best oil is that which distils over during the first hour of the process. The finest French oil comes from the departments Gard and Hérault, and the neighbourhood. The supply of oil from the Dalmatian islands is somewhat irregular, and, according to Schimmel & Co., the reason of this is that the rosemary woods, as they are called, are municipal property, and are leased to the peasants and distillers, but with an effective control as to harvesting. This follows a regular rotation, the general crop being gathered in one year and very sparing crops for the next two years. The richest plants grow on the island of Solta, but the successful cultivation of vineyards has nearly replaced the rosemary industry. A little is cultivated on the island of Lissa, but the majority comes from Lesina. The total pro-

duction of these islands varies from 15,000 to 50,000 lb. per annum. The plants are usually sun-dried before distillation, and the process is carried out in very primitive apparatus, which facts possibly account largely for the inferior quality of the oil. The adulteration practised on this oil appears to commence at Trieste, and not on the islands. The usual adulterants are turpentine and petroleum oils, although the finer qualities are at times adulterated with spike oil. The chief employment of this oil is in perfumery, the well-known *Eau de Cologne* containing oil of rosemary. It has also a limited use in pharmacy, being used, for example, to perfume the official soap liniment, and it is official in the *British Pharmacopœia*. This authority requires that the oil shall have a specific gravity ·900 to ·915, to be dextro-rotary to + 10°, and to be soluble in 2 volumes of 90 per cent. alcohol. Cripps (*Ph. Journal*, xxi., p. 937) states that English oil has a specific gravity of ·901 to ·924, whereas foreign oil varies from ·881 to ·907; and that the English oil is laevo-rotary. These observations do not appear to have been carried out altogether on reliable oils, for genuine rosemary oil, whether English or foreign, should never have a specific gravity below 0·896. The limits ·896 to ·920 may be regarded as covering all genuine oils, which are usually dextro-rotary from + 1° to + 12°. The solubility in alcohol is also important, as the chief adulterants, turpentine and petroleum are much less soluble than the pure oil. Genuine rosemary oil should dissolve in from ½ to 2 volumes of 90 per cent., and in 10 volumes of 80 per cent. alcohol, with at most a slight turbidity: some samples are far more soluble than others. The presence of much petroleum oil is also indicated by evaporating the oil in a water bath, when pure rosemary oil should only leave a slight resinous residue, whilst the petroleum (necessarily the higher fractions of petroleum oil, in order not to unduly interfere with the specific gravity) will

be left unvolatilised. The addition of alcohol to the oil may be detected by the addition of a crystal of magenta to the oil dried over calcium chloride. The dye is insoluble in the oil, but imparts a pink colour to it if alcohol be present. Fractional distillation, however, with appropriate tests for alcohol to the first distillate, is better.

Schimmel & Co. propose the distillation of the first 10 per cent. of the oil and examination of its rotatory power. Pure oils, they state, invariably yield a dextro-rotary fraction. Five samples distilled by themselves gave the following results:—

	Yield.	*Specific Gravity.*	*Rotation.*	*Rotation of first 10 per cent.*
1 .	1·4 per cent.	·913	+ 4° 16′	+ 1° 30′
2 .	1·7 ,,	·909	+ 3° 40′	+ 1° 22′
3 .	1·5 ,,	·910	+ 5° 54′	+ 6° 26′
4 .	1·73 ,,	·904	+ 6° 54′	+ 7° 49′
5 .	1·73 ,,	·906	+ 8° 52′	+ 8° 24′

The author and Bennett, however, have recently shown that pure rosemary oil may be laevo-rotary and yield laevo-rotary fractions on distillation. As those deductions were made, on oils distilled from the plant, by the authors, the following full details are reproduced from the original paper (*Chemist and Druggist*, 1906, 137):—

It has been observed for some time past that rosemary oil of Spanish origin is frequently laevo-rotatory, and it has been assumed that this is due to adulteration. Gildemeister and Hoffmann, in their book on essential oils, state that pure rosemary oil is always dextro-rotatory, and, further, that the first 10 per cent. distilled is likewise dextro-rotatory. Messrs. Schimmel & Co. in a recent report state that they have observed a dextro-gyrate oil giving a laevo-gyrate fraction on distilling the first 10 per cent., and consider that this was due to the admixture of other plants with the rosemary. We have recently carried out investigations which throw some light on this matter, the results of which are here given.

We have had consigned to us authentic specimens of rosemary herb grown in Spain and France respectively (some 300 lb. in all), and the oil from these has been distilled in the laboratories of Messrs. Wright, Layman & Umney, Limited, under the direct supervision of Mr. J. C. Umney. We are also indebted to Mr. H. E. Burgess for the distillation of one sample. The results of our examination of these oils prove beyond doubt that a laevo-rotatory oil is

consistent with purity, and also a dextro-rotatory oil giving laevo-rotatory fractions.

It is customary in France to distil the oil from herb which has been collected after the flowering period (February and March) and dried for about eight days in the sun. In Spain the distillation goes on all the year round, and some variation is therefore to be expected. Both fresh and dried herbs are employed, the latter when the supply is greater than the capacity of the stills and when it has to be carted from a long distance. In the dry state the leaves can be readily separated from the stalks by threshing, but in the fresh condition it is impossible so to separate them. The yield from the fresh herb is from 0·4 to 0·75 per cent., while the dried leaves yield about 1 per cent. of oil, which is of finer quality than that from the fresh herb. The characters of three typical samples were as follows:—

———	1 (Spanish).	2 (French).	3 (French).
Source	Leaves alone	Leaves and stalks	Leaves alone
Specific gravity	0·917	0·897	0·914
Optical rotation	+5° 30′	−8° 30′	−3°
Esters calculated as bornyl acetate	3·2 °/°	3·0 °/₀	3·6 °/₀
Total borneol	19·7 °/°	10·9 °/₀	18·5 °/₀
Optical rotation of first 10 per cent. (100 mm.)	−1°	−12° 30′	−10°

No. 1 was distilled from herb collected towards the end of last summer and dried in the sun. It consisted entirely of leaves which were well developed and of a fine green colour. The yield was 0·89 per cent.

No. 2 was distilled from stalky herb in the dried condition, collected in February last. The proportion of stalks amounted to nearly 60 per cent. Yield of oil 0·4 per cent.

No. 3 was distilled from the same consignment as No. 2, but the stalks were separated and the leaves alone distilled. They yielded 1·09 per cent. of oil, containing a high proportion of borneol. The leaves were somewhat discoloured, probably owing to some fermentation having taken place.

The stalks alone yielded very little on distillation, showing that they contain a much smaller percentage of oil and that of little odour value. Our results show that the laevo-rotatory constituent (laevo-pinene) occurs in greater proportion when the stalks are included, and that an inferior oil is then obtained. It is evident that oils derived from carefully picked leaves yield fractions which are laevo-gyrate.

The following are the results of fractionation of the above oils:—

No. 1.

Fraction.	Sp. Gr.	Rotation.	Refractive Index.	B.P. commencing at
	%			
1. . .	10	0·884	−1°	1·4676	152° C.
2. . .	10	0·890	−1° 10′	1·4680	156° C.
3. . .	10	0·895	−1° 20′	1·4681	159° C.
4. . .	10	0·902	+1°	1·4682	162° C.
5. . .	10	0·908	+1° 20′	1·4683	163° C.
6. . .	10	0·911	+2°	1·4686	165° C.
7. . .	10	0·922	+2° 30′	1·4700	169° C.
8. . .	10	0·940	+3°	1·4736	177° C.
Residue	20	Partially crystallised		1·4885	185° C.

No. 2.

Fraction.	Sp. Gr.	Rotation.	Refractive Index.
	%		
1	10	0·874	−12° 30′	1·4660
2	10	0·878	−13°	1·4670
3	10	0·879	−13° 30′	1·4670
4	10	0·883	−12° 20′	1·4670
5	10	0·886	−11° 20′	1·4670
6	10	0·891	−10° 30′	1·4670
7	10	0·896	−8° 30′	1·4678
8	10	0·909	−5° 30′	1·4702
Residue . .	20	—	—	1·4859

No. 3.

Fraction.	Sp. Gr.	Rotation.	Refractive Index.
	%		
1	10	0·885	−10°	1·4660
2	10	0·888	−10°	1·4680
3	10	0·891	−9° 20′	1·4685
4	10	0·896	−7° 70′	1·4686
5	10	0·900	−6° 70′	1·4686
6	10	0·909	−4° 50′	1·4686
7	10	0·921	−1°	1·4686
8	10	0·938	+2°	1·4697
Residue . .	20	Partially crystallised		—

It is therefore quite clear that the borneol is derived principally if not entirely from the leaves, and a genuine laevo-rotatory oil containing a comparatively low percentage of borneol may be assumed to have been distilled from both leaves and stalks, since the leaves alone yield an oil which has a finer odour and higher borneol content.

These facts have been confirmed by Birckenstock.

The estimation of the esters and free alcohols, by saponification and acetylation with a second saponification, yields valuable information. The results are expressed as borneol and bornyl acetate. According to Schimmel & Co., about 16 to 19 per cent. of borneol and 5 to 6 per cent. of bornyl acetate are present. Laevo-rotary oils may contain as little as 10 per cent. of borneol. When fractionally distilled not a great deal should come over under 155°. The quantity will naturally vary according to the form of apparatus used, but under no circumstances should more than 15 to 20 per cent. be obtained. Adulteration with turpentine is probable, if as much as this distils over.

According to Haller (*Comptes Rendus*, cviii., p. 1308), the "camphor" of rosemary oil consists of *dextro*-camphor, *laevo*-camphor, *dextro*-borneol and *laevo*-borneol. Esters of borneol are also present, chiefly the acetate. Hirschsohn found cineol in the oil, and Schimmel & Co. have identified the presence of pinene and camphene. The pinene appears to be present, partly at all events, as *dextro*-pinene. The statement of Brannt (*Animal and Vegetable Fats and Oils*, vol. ii., p. 570) that "rosemary oil consists of a *laevo*-terpene (80 per cent.) which may probably be entirely *laevo*-pinene" is entirely erroneous, and evidently based on the examination of adulterated samples.

Peppermint Oil.—This important oil is the product of the distillation of the herbs *Mentha piperita* and *Mentha arvensis*, the latter producing the "Japanese" oil and the former all the other distillates.

Commercially, peppermint oil appears to have commenced

its history about 1750, when cultivation was commenced at Mitcham in Surrey. To-day the English peppermint fields are chiefly located in this district, and in the neighbourhoods of Market-Deeping in Lincolnshire, Hitchin in Hertfordshire, and Wisbeach in Cambridgeshire. The oil produced by English-grown plants bears the same relation to most of the foreign oil, as is the case with lavender oil, although it is claimed that certain distillates of German plants approach the English variety in fineness of odour, as they certainly do in price. Distillation of the oil in America, which is now the most important producer of peppermint oil, commenced in the early part of last century, when a small distillery was erected in Wayne County, New York State. To-day many thousand acres are under cultivation, and the principal districts producing the oil are Wayne County (New York), various portions of the State of Michigan, especially Wayne County (Michigan), Van Buren, St. Joseph's and Kalamazoo Counties; St. Joseph's County, Indiana; and to a smaller extent in some of the counties of Ohio and in some parts of the south of the Canadian province Ontario. The whole of the peppermint cultivation in America is thus confined to the north-east portion of the United States and extreme south of Canada. In Germany, plantations have been successfully established at Miltitz, in the neighbourhood of Liepzig, by Messrs. Schimmel & Co., and a fine oil is obtained from the plants grown there. A small quantity of oil is also produced in France, in the departments of the Yonne and du Nord. Japan and, to a certain extent, China produce large quantities of peppermint oil. Mr. E. M. Holmes identified the Japanese plant as *Mentha arvensis*, and as the Chinese plant differs slightly from the Japanese, he retains, for the sake of distinction, the names *Mentha arvensis var. piperascens* for the Japanese, and *Mentha arvensis var. glabra* for the Chinese plant. The chief Japanese plantations are located north of Yokohama, and southwards into the pro-

vinces of Bingo-Bitchin. The largest centre of cultivation is in the province of Uzen, which produces more oil than all the other provinces put together. Uzen is in the north-east of the island of Hondo, the chief of the Japanese islands. After Uzen, Bingo is the most important producing province. The following map (reproduced by the courtesy of the editor of the *Chemist and Druggist*) illustrates the chief peppermint districts in Japan :—

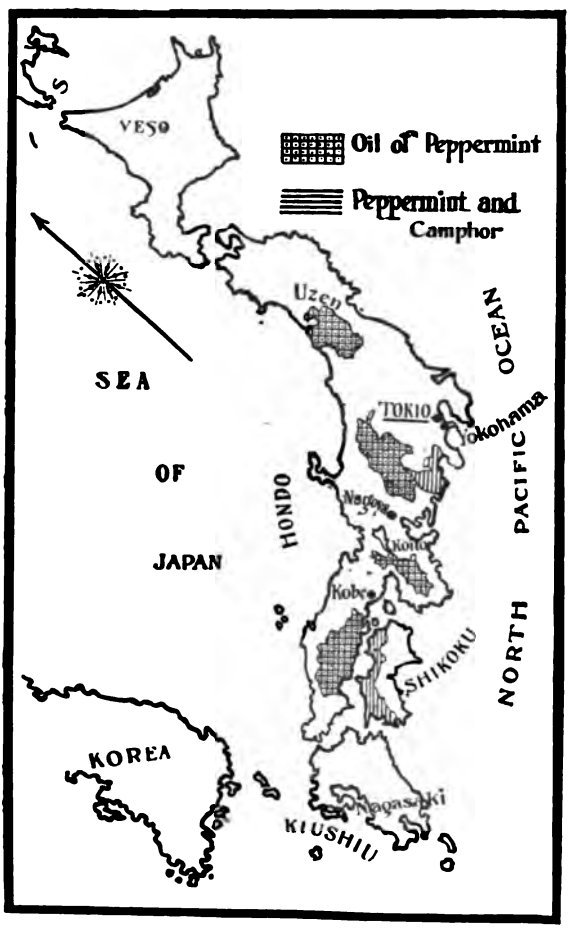


FIG. 17.

In England two varieties of the plant are grown, known as "black" and "white" mint. Of these the former is the coarser plant, rarely flowering in England, and yielding rather more oil of somewhat less delicate aroma than the white mint. The herbs are distilled in the green state, although sometimes left for a day or two in heaps, after being cut. In England most of the stills used hold from 4 to 8 cwt. of herbs, and have a false bottom which is covered to the depth of 2 feet with water, and direct heat is then applied. The distillation is carried on for about five hours. The yield varies according to the season from about ½ to 1 per cent.

In America the mint is usually left in the sun in small cocks for a short time before distillation. With regard to the advisability of drying the plants before distillation, thus reducing the bulk and so increasing the charge of a still, Mr. Todd, a well-known Michigan grower, carried out experiments on a very large scale, and came to the following conclusions:—

1. No loss of essential oil of peppermint through diffusion in the atmosphere is occasioned by thorough drying of the plants and prolonged exposure to atmospheric action prior to distillation.

2. Such exposure does not increase the crystallising tendency of the essential oil.

3. A heavy and insoluble resinoid is produced by oxidation, increasing the specific gravity of the oil and affecting the boiling point and solubility, by raising the former and decreasing the latter.

4. To obtain the best results as to the quality of oil produced and the facility of handling and distillation, the plants should be dried as thoroughly as possible without endangering the loss of leaves and blossom; distillation should then take place as soon as convenient to prevent the formation of resin.

A common form of still used here is a wooden tub or vat made of well-seasoned wood, well hooped with iron. Two are kept side by side, so that one can be used whilst the other is being emptied. The mint is packed into the vat, being trodden down well with the feet, and a steam-tight cover screwed on. Steam is supplied from a boiler to the bottom of the vat, usually at a pressure of from 30 to 40 lb., and the oil and steam are condensed in a worm condenser.

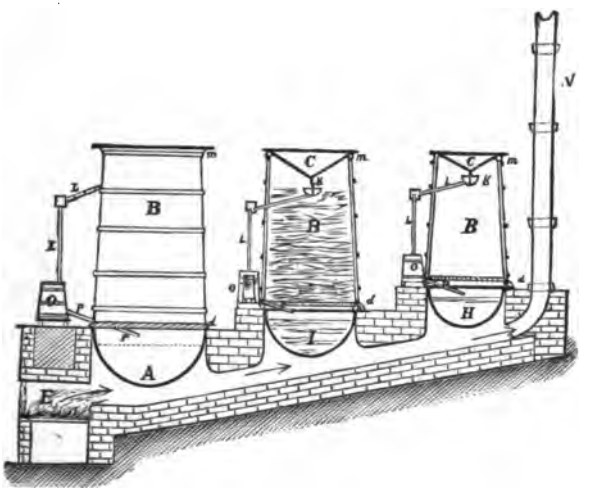


FIG. 18.—Peppermint Stills (section).

The following details of the method of distillation used in Japan are from a paper published by Mr. E. Marx (*Mitt. der deutschen Gesselschaft für Natur. und Völkerkunde Ostasiens*, vol. vi., p. 335) and translated in the *Chemist and Druggist* (25th April, 1896):—

"From this report we learn that the industry has not benefited by the introduction of European methods, although it is a considerable one. It is Mr. Marx's opinion that the substitution of an improved method for that now followed would benefit both the quantity and quality of the oil produced. The apparatus universally adopted in Japan consists of

cast-iron broad-edged boilers, A, I, H; wooden vats, B; and condenser, C. Generally there are three sets of stills, etc., combined in one battery with a common furnace. They are arranged in steps, so that the lowest is built into the ground.

"The process is begun by filling the boilers, A, I, H, with water; then the vats, B, which have perforated bottoms, are placed on the broad edges and surrounded with straw bands and soft clay. It is in these vats that the peppermint is placed. Next, the inverted condenser, C, is put on and filled with water and the furnace, E, lighted. The heat passes

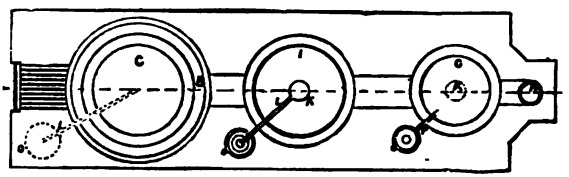


FIG. 19.—Peppermint Stills (ground plan).

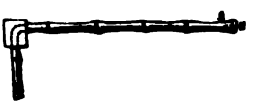


FIG. 20.—Bamboo Syphon.

from E below A, I, and H, and disappears through the chimney, N, on which the distilling begins. The boilers, I and H, are properly heated by the fumes as they pass, and sufficiently so, as H is smaller than I, and I smaller than A. The steam, penetrating the herb, carries with it the essential oil, and condenses on the outer side of C, being collected in the vessel, K, hanging upon it, from which the condensed water containing the oil passes through a bamboo reed, L, inserted in K to the florentine flasks, O. Each of these consists of a little wooden container in which a glass cylinder (an old bottle without bottom or neck) is inserted. In this, the water separated from the oil runs through the little pipe, P,

again into the boilers, A, H, I. As soon as the water in C becomes hot, the workman replaces it with cold water. The emptying is effected by a bamboo syphon. The workman inserts the short arm in the inverted cooler, closes the lower opening and sucks the syphon until the water flows into it. According to the inborn easy-going nature of the Jap workman, who likes to pause in his work for a smoke, it often happens that the cooling water in C begins to boil and steam runs through instead of the condensed water saturated with oil, so that the atmosphere in the neighbourhood becomes so impregnated with peppermint that any one near loses sight and sense of smell. The workman does not go unpunished, as he burns his mouth by sucking up the boiling water; that, however, does not prevent him from going on smoking, and the same thing happens again. In addition to the direct loss of oil caused by this negligence, it often happens that the water-boiler becomes dry, and then the herb in the still is burnt, in spite of the straw. This sometimes happens in spite of all precautions, as the flames frequently overheat the boilers if the water runs too low, and the products of burning straw get over with the distillate, which explains why Japanese peppermint oil sometimes has a peculiar empyreumatic flavour."

Japanese oil of peppermint contains a very high proportion of menthol, which is frequently removed, and the dementholised oil sold either as such, or, fraudulently, as the natural oil. The usual manner in which the menthol is obtained is by a simple process of freezing, whereby the crystals separate, and are freed from the adherent oil either by pressure or centrifugal treatment. To purify them they should be recrystallised from a suitable solvent, such as alcohol. If it is wished to extract the maximum quantity of menthol, it is advisable to distil off the terpenes, etc., under reduced pressure, and then freeze the residual oil.

Peppermint oil has an extensive use in the preparation of confectionery, liqueurs, etc., and in pharmacy. It is official in the *British Pharmacopœia*, which requires it to have a specific gravity of ·900 to ·920, and to be soluble in four times its volume of 70 per cent. alcohol. An unsatisfactory qualitative test for menthol is also added; the oil when cool deposits crystals of menthol, it being allowed to add a crystal of this body to induce the crystallisation. This should be replaced by a quantitative determination of the menthol.

Peppermint oil is one of those which improve by keeping, the aroma becoming more delicate, even when kept for ten or twelve years.

Menthol has long been known as the chief constituent of oil of peppermint, and although all the oils of peppermint have not been thoroughly examined, it is probable that the same bodies are in general present in all of them, except in so far as small quantities of some compound or compounds may be present in special oils, modifying the aroma to a considerable extent. For example, the precise difference in the composition of American and English oils is not completely understood. Andres (*Chem. Centr.*, 1890, ii., p. 63) showed that the oil obtained from plants grown in Russia contained the terpene limonene $C_{10}H_{16}$, the hydrocarbon menthene $C_{10}H_{18}$ (which can also be obtained by the dehydration of menthol), menthol $C_{10}H_{19}OH$, and menthone $C_{10}H_{18}O$. Power and Kleber, in 1894, carried out a lengthy investigation of American oil of peppermint, and showed that it contained the following bodies:—

Acetic Aldehyde $CH_3.COH$.
Acetic Acid $CH_3.COOH$.
Pinene (*inactive*?) $C_{10}H_{16}$.
Limonene (*laevo*?) $C_{10}H_{16}$.
Menthone $C_{10}H_{18}O$.
Menthyl Acetate $C_{10}H_{19}.C_2H_3O_2$.
Cadinene $C_{15}H_{24}$.
A Menthyl ester $C_{10}H_{19}.C_8H_{11}O_2$.
Iso-valeric Aldehyde $C_4H_9.COH$.
Iso-valeric Acid $C_4H_9.COOH$.
Phellandrene $C_{10}H_{16}$.
Cineol $C_{10}H_{18}O$.
Menthol $C_{10}H_{19}.OH$.
Menthyl-iso-valerate $C_{10}H_{19}.C_5H_9O_2$.
A Lactone $C_{10}H_{16}O_2$.

Traces of amyl alcohol and dimethyl sulphide are said to exist in the oil. Charabot in examining French peppermint oil confirmed the presence of acetic and valeric (iso-valeric?) acids in the form of esters.

For the chemical examination of peppermint oil, the following characters must be determined. Specific gravity, optical rotation, percentages of free menthol, combined menthol as esters, and of menthone, solubility and (as yielding confirmatory information) behaviour on distillation. Peppermint oil from *Mentha piperita* should have a specific gravity ·900 to ·920, rarely rising to ·925, and an optical rotation usually between – 23° and – 33°, but falling to – 10° or even lower in rare cases. Italian and French oils are sometimes outside these limits. The refractive index is about 1·4650.

The Japanese oil from *Mentha arvensis* has a specific gravity of ·895 to ·905, and an optical rotation of – 25° to – 43°. Peppermint oil should be soluble, at most with a trifling opalescence, in 4 volumes of 70 per cent. alcohol. The method of estimating the menthol (or isomeric menthols —which are possibly present) and the menthone is by the saponification and acetylation process which was first applied to this oil by Power and Kleber. The total quantity of menthol as esters is first estimated by a preliminary saponification. A quantity of the oil is then saponified and the resulting oil, free from esters, separated and dried. By acetylating this, the menthol is completely converted into menthyl acetate and is estimated by another saponification. This gives the total menthol (in the ester free oil). Another portion of the ester free oil is reduced by means of sodium and alcohol (thus converting the menthone into menthol), and then acetylated and saponified. The amount of menthol now found corresponds to the total menthol originally in the oil together with that formed by reducing the menthone (the

difference in the molecular weights of menthol and menthone may here be neglected). The following are the details of the process as given by Power and Kleber :—

About 20 grammes (accurately weighed) of peppermint oil, together with 30 c.c. of an alcoholic normal solution of sodium hydroxide, are either heated to boiling for an hour in a flask provided with a reflux condenser, or the mixture, contained in a strong, securely stoppered glass bottle, is heated for an hour in a bath of boiling water, and subsequently the uncombined alkali titrated with normal sulphuric acid with the use of phenol-phthalein as an indicator. From this the combined menthol is calculated as menthyl acetate.

The saponified oil is then repeatedly well washed with water and finally boiled for an hour with an equal volume of acetic anhydride and 2 grammes anhydrous sodium acetate in a flask provided with a suitable condensing tube, ground at one end so as accurately to fit the neck of the flask. The product, after cooling, is washed with water, then with a dilute solution of sodium hydroxide, dried in contact with calcium chloride, and filtered. From 8 to 10 grammes of the resulting oil are then saponified as above, with the use now of 50 c.c. of alcoholic normal solution of sodium hydroxide, and the uncombined alkali determined by titration.

As each cubic centimetre of normal alkali required for saponification corresponds to 0·156 gramme menthol, and as this yields 0·198 gramme menthyl acetate, it is necessary in order to calculate the found amount of menthol with reference to its percentage in the non-acetylised oil (free from ester) to subtract from the amount of oil used for saponification 0·042 gramme (the difference between 0·156 and 0·198 gramme) for each cubic centimetre of normal alkali consumed. If, for example, s grammes of acetylised oil had required for saponification a c.c. of normal alkali, the total percentage P

of menthol, free and in the state of ester, may be calculated by the following formula:—

$$P = \frac{a \times 15{\cdot}6}{s - (a \times 0{\cdot}042)}$$

This, indeed, does not indicate with absolute exactness the percentage of menthol contained in the original oil, for it is assumed in this calculation that all the menthol which is present as ester is combined with acetic acid, whereas as a matter of fact it is partly in combination with iso-valerianic acid, etc. But the error so introduced is so small that it may be left out of account.

As menthone may readily be converted into menthol by reduction, the above-described method may be also employed for the determination of the amount of menthone in the oil, in the following manner. The oil is saponified, and in a portion of the product, previously deprived of alcohol, the percentage of menthol is determined. Another portion is diluted with twice its volume of alcohol, and treated at the boiling temperature of the liquid with metallic sodium. Of the oil which separates by the subsequent addition of water, a weighed quantity is used for another estimation of menthol. The increase corresponds to the amount of menthone present.

The above formula, which gives the total percentage of menthol, is not quite accurate, as it is referred to the ester free (saponified) oil. The correction necessary to be introduced is not of great importance, as the quantity of menthyl esters is not nearly so great as that of free menthol, but to be perfectly correct it must be remembered that to calculate the ester free oil to the original peppermint oil, the latter has lost weight as compared with the former to the extent of ·75 per cent. for 1 each per cent. of KOH required for the preliminary saponification of the esters, assuming that these

are all present as menthyl acetate. Thus if an oil gives an ester content of 10·6 per cent., equivalent to 3 per cent. of KOH, or 8·4 per cent. of menthol, and a total menthol content as calculated from the above formula of 60 per cent., it is necessary to multiply this by the factor $\frac{100}{102{\cdot}3}$ to obtain the total menthol content in the original oil, *i.e.*, 58·7. Hence the free menthol will be 50·3 per cent., and the combined menthol 8·4 per cent.

With regard to the fractional distillation, it may be noted that the results are very variable, according to the exact conditions of the experiment. But an oil with high menthol content will always give a considerable distillate in the neighbourhood of 215°, which is near the boiling point of menthol (212°).

The majority of the accompanying figures for a number of oils are given by Schimmel & Co.

In general, English oils have a specific gravity of about ·906 to ·909, and an optical rotation of – 27° to – 32°, and contain from 60 to 70 per cent. of menthol, or rather more than most American oils. Japanese oils often contain in the natural condition as much as 85 per cent. of menthol. Umney has examined samples of "black" and "white" mint oils comparatively, and gives the following figures for them :—

		Sp. Gravity.	*Rotation.*	*Menthol—* *as esters.*	*free.*	*Menthone.*
1	Black	·9096	– 23·5°	3·7	59·4	11·3
2	White	·9058	– ·33°	13·6	51·9	9·2

It is necessary to examine a number of samples before generalising on these results.

Charabot has examined a number of French oils (*Bull. Soc. Chim.*, xix., p. 117) which were characterised by their low rotation. His figures are as follows :—

	Sp. Gravity.	*Rotation.*	*Menthol—* *as esters.*	*free.*	*Menthone.*
1	·921	− 6° 38′	6·6	39·4	9
2	·918	− 6° 40′	5·6	38·7	8·9
3	·918	− 5° 54′	8·0	35·7	8·8
4	·918	− 7° 6′	7·7	37·8	9·6

Zay gives the following figures for six samples of Italian oil:—

	$d_{15°}$.	$\alpha_{d16°}$.	$n_{d16°}$.	*Total menthol.* %	*Ester-menthol.* %	*Free menthol.* %
I.	0·916	− 2° 34′	1·468	55·5	9·72	45·78
II.	0·9171	− 10° 41′	1·467	58·6	7·10	51·5
III.	0·9256	− 7° 4′	1·468	45·0	6·01	38·99
IV.	0·9122	− 16° 21′	1·46733 (20°)	52·5	7·89	44·61
V.	0·916	− 13° 17′	1·46783 (20°)	53·07	9·66	43·41
VI.	0·9157	− 12° 34′	1·46783 (20°)	50·95	9·87	41·08

Schimmel & Co. give the following figures for three samples of French oil:—

Specific gravity . . .	0·9249	0·9108	0·9120
Rotation	− 5° 20′	− 17° 46′	− 35° 18′
Total menthol . . .	45·75 %	50·82 %	69·26 %

Wielen has examined a Javanese oil of peppermint distilled from *Mentha javanica*. Its specific gravity was 0·9214 and optical rotation + 4° 40′. It contained much pulegone, but little menthol.

Umney and Bennett examined some oils distilled from plants of English origin grown in Sicily.

The oils varied in character with the season of distillation as follows:—

	Sp. gr.	*Rotation.*	*Menthol.*
July oil, 1904 . .	0·908	− 14°	40 %
December oil, 1904 .	0·920	− 23°	70·5 %
July oil, 1905 . .	0·906	− 21°	41·6 %

There is one general conclusion that may be fairly drawn from all these figures; that is, that the effects of climate, soil and cultivation have a very marked influence on the quality and composition of peppermint oil. For mixtures

Designation of the Oil.	Specific Gravity at 15° C.	Optical Rotation in a 100 mm. tube.	Menthol in the form of Esters.	Free Menthol.	Total Menthol.	From 50 ccm. of Oil there distil in ccm. between the temperatures noted:								
						1 to 200° C.	200-205°	205-210°	210-215°	215-220°	220-225°	225-230°	230-235°	Residue
			%	%	%									
I. F. B., from dry herb	0·9140	− 32° 0′	14·12	45·5	59·6	1·3	1·2	4·3	9·4	12·0	9·8	4·5	1·3	6·1
Ia. F. B., from fresh herb	0·9130	− 30° 0′	11·25	43·2	54·5	0·6	1·2	5·7	8·5	11·6	9·2	4·2	2·2	6·7
Ib. Wayne Co., N.Y., '92	0·9158	− 26° 45′	9·32	40·8	50·1	1·4	1·8	6·3	10·0	12·9	7·3	2·4	1·8	6·3
Ic. „ „ '93	0·9110	− 32° 30′	9·04	46·1	55·1	1·1	1·4	5·0	10·7	13·9	7·6	2·9	1·6	5·4
Id. „ „ twice rectified (F. S. & Co.)	0·9110	− 32° 45′	8·61	51·0	59·6	1·5	3·7	8·8	14·7	12·2	4·2	—	—	5·2
Ie. V. B. Co., Mich., '93	0·9067	− 29° 20′	6·39	43·6	50·0	1·9	5·0	9·4	13·2	12·4	2·3	—	—	5·1
If. Wayne Co., Mich., '93	0·9135	− 28° 30′	7·73	50·3	58·0	1·7	1·6	5·5	9·6	12·2	8·9	3·2	3·1	5·8
II. St. J. Co., Mich., '93 (I.)	0·9135	− 9° 45′	3·63	28·9	32·6	1·9	2·6	12·0	14·0	11·6	4·4	—	—	3·3
IIa. „ „ '93 (II.)	0·9083	− 19° 30′	4·23	29·6	35·8	3·4	7·0	7·6	13·2	10·1	3·3	1·5	—	4·1
IIb. "Rose Mitcham" } Michigan	0·9050	− 28° 35′	4·87	44·2	48·6	4·4	9·6	13·4	17·1	8·2	—	—	—	2·5
IIc. "Crystal White" } Michigan	0·9105	− 23° 55′	6·74	44·2	50·9	1·7	5·8	9·9	15·4	9·4	3·4	—	—	4·1
IId. "Redistilled Oil" } Michigan	0·9105	− 23° 30′	8·59	46·5	55·1	3·3	6·5	8·1	8·8	9·9	5·2	—	—	8·7
III. Mississippi	0·9250	− 13° 40′	11·47	24·2	35·7	0·9	0·3	1·2	6·5	16·2	11·8	4·8	2·4	6·6
IV. Japanese, normal	0·9100	− 34° 45′	3·45	72·7	76·2	0·7	0·4	3·4	22·0	17·2	2·1	1·0	—	3·5
V. „ dementholised	0·9080	− 31° 20′	5·71	55·1	60·8	0·5	1·6	10·2	20·7	12·0	3·3	—	—	2·4
VI. Mitcham	0·9070	− 27° 55′	4·92	53·9	58·8	1·4	0·7	12·2	24·7	8·6	—	—	—	3·7
VII. Saxon	0·9100	− 26° 0′	6·38	61·2	67·6	1·7		10·9	21·3	11·6	2·1	—	—	2·1
Russian oil	0·905-0·915	− 17° to − 22°	5	45	50	—		—	—	—	—	—	—	—
French oil	0·918-0·921	− 6° to − 10°	5-10	35-40	45-50	—		—	—	—	—	—	—	—
Italian	0·912-0·925	− 2° to − 16°	10	46	50-60	—		—	—	—	—	—	—	—

of the various kinds of these oils, the nose of an experienced dealer is the best test, as a chemical examination, whilst deciding on the purity or otherwise of the oil, will often fail to discriminate between various blends.

Peppermint oil is frequently adulterated. The American oil is sometimes enriched by the addition of Japanese menthol, which is usually cheaper than American oil. Camphor oil is used as an adulterant; also petroleum at times. The author and Bennett have found cedar-wood oil and oil of African copaiba used as adulterants (see below). Bennett has found the tri-acetin in one sample. The behaviour on distillation as compared with normal samples affords the surest indication of such adulteration. The following table represents a normal distillation of pure oil:—

PURE OIL.

(Sp. gr. 0·911; Ref. Index 1·4645.)

Quantity.	*Sp. Gr.*	*Rotation.*	*Ref. Index.*
%			
12½	0·898	−10°	1·4660
12½	0·903	−14°	1·4635
12½	0·907	−16°	1·4645
12½	0·910	−20°	1·4640
12½	0·912	−23°	1·4615
12½	0·912	−23°	1·4615
12½	0·915	−34°	1·4630
12½	0·962	—	1·4790

An oil containing tri-acetin gave the following results (Bennett):—

Fractions.	*Quantity.*	*Sp. Gr.*	*Rotation.*	*Ref. Index.*
	%			
1 . .	12½	0·900	− 15°	1·4645
2 . .	12½	0·902	− 15°	1·4670
3 . .	12½	0·910	− 14°	1·4650
4 . .	12½	0·920	− 16°	1·4640
5 . .	12½	0·926	− 20°	1·4640
6 . .	12½	0·938	− 22°	1·4640
7 . .	6	—	—	1·4640
Residue .	19	1·147	—	1·4450

With cedar-wood and copaiba oils, the high boiling fractions are found to have very high refractive indices (up to 1·4900 or even 1·500), and in the case of African copaiba, cadinene is found in the fraction 255° to 270°, and in the case of cedar oils, the corresponding fraction may be laevo-rotary to the extent of − 45°.

As indicating the behaviour of African copaiba oil, which has been used to an enormous extent for adulterating this oil, the following figures for the pure copaiba oil are of interest. A sample of the balsam itself was distilled by the author and Bennett and the oil collected in four equal fractions.

The figures obtained were:—

	Sp. Gr.	*Rotation.*	*Ref. Index.*
1	0·917	+ 17° 30′	1·5080
2	0·918	+ 28° 30′	1·5043
3	0·921	+ 46°	1·5061
4	0·927	+ 55°	1·5082

Other samples of African copaiba oil had the following characters:—

Specific gravity	0·919 – 0·932
Rotation	+ 30° – + 37°
Refractive index	1·4999 – 1·5040

Two of these on fractionation showed variation of optical rotation and refractive index as under:—

	I.		II.	
	Rotation.	*Ref. Ind.*	*Rotation.*	*Ref. Ind.*
25 per cent. . .	+ 16°	1·4960	+ 24°	1·4975
25 „ . .	+ 19°	1·4965	+ 26°	1·4980
25 „ . .	+ 24°	1·4980	+ 29°	1·4981
20 „ . .	+ 48°	1·5089	+ 43°	1·5090
5 „ residue	—	—	—	—

Spearmint Oil.—This oil is distilled from the green herb *Mentha viridis*, which yields under ½ per cent. of oil. The spearmint oil of commerce, however, is largely obtained from *Mentha crispa*, but it is practically identical with that from *Mentha viridis*.

So far back as 1864, Gladstone stated that this oil con-

sisted of carvone and a terpene. The results of Trimble and Baeyer confirm this statement, and so far but little further is known of the chemistry of this oil. The *British Pharmacopœia* describes it as being distilled from *Mentha viridis*, and having a specific gravity of ·920 to ·940. Schimmel & Co., however, state that an oil distilled by themselves in America had a specific gravity of ·980, and consider that commercial oils may owe their lower gravity to the fact that the heavier oil is usually left in the still and only the lighter oil collected. This suggestion, however, is most improbable.

A fractional distillation shows a large fraction at 220° to 226°, indicating a high proportion of carvone, usually from 35 to 45 per cent. The optical activity is high, often reaching as much as − 40° or − 50°. The oil should dissolve in an equal volume of 90 per cent. alcohol. This oil is scarcely ever employed in pharmacy, but is used to a limited extent for flavouring and perfumery. The English oil is very expensive, and scarcely ever used, the majority of the oil of commerce being derived from America. A Russian oil of spearmint recently appeared on the market, differing entirely from the ordinary oil. Possibly it is the product of *Mentha aquatica*, or a mixture of this and other species. Its specific gravity was about ·880 to ·890 and optical rotation from − 20° to − 25°. A sample was examined by Schimmel & Co., and gave the following results. Specific gravity, ·885; optical rotation, − 23° 12′; soluble in two volumes of 70 per cent. alcohol; required 2·6 per cent. of KOH for saponification, and gave an alcohol number calculated as $C_{10}H_{18}O$, by the acetylation process, of 40·6 per cent. The constituents identified were—*laevo*-carvone (5 to 10 per cent.), *laevo*-linalol (50 to 60 per cent.), cineol and *laevo*-limonene (20 per cent.). Other mint oils of little importance are the following:—

Mentha aquatica yields an oil of specific gravity ·880 to

·890 and of variable optical rotation. *Mentha canadensis* yields an oil of specific gravity ·940. Horsemint oil is the product of the American plant *Monarda punctata* (*Mentha sylvestris* is known in England as horsemint, but its oil is unknown). This oil is a slightly dextro-rotary liquid of specific gravity ·930 to ·940. It contains a considerable quantity of terpenes including dextro-limonene together with cymene, thymol (25 per cent.), an alcohol of the formula $C_{10}H_{18}O$ (linalol ?), and traces of formic, acetic and butyric acids.

There are a few other oils of the Monarda species which may be conveniently tabulated here.

Monarda Fistulosa.—This oil contains carvacrol, thymoquinone and thymo-hydroquinone. It has a specific gravity 0·915 to 0·941 and is slightly laevo-rotary. The carvacrol is present to the extent of 50 to 60 per cent.

Monarda Didyma.—This oil has a specific gravity about 0·902 and optical rotation − 10°. It (probably) is free from both thymol and carvacrol.

Monarda Citriodora.—This oil has a specific gravity 0·945, and contains 1·2 per cent. of citral. It also contains 65 per cent. of phenols, of which carvacrol is the principal, with some hydro-thymoquinone.

Monarda Myristica.—This oil has a specific gravity 0·896 and optical rotation − 65°. It contains limonene, traces of phenols, phellandrene and probably myristicol.

Pennyroyal Oil.—The leaves and other parts of the plant *Mentha pulegium* yield the ordinary pennyroyal oil. This plant is a native of most parts of Europe, the Caucasus, Chili, Teneriffe, etc. The volatile oil is of a yellow or greenish-yellow colour, and possesses a strong odour of the plant. The specific gravity varies from ·930 to ·960 and the optical rotation from + 16° to + 25°. It is soluble in two volumes of 70 per cent. alcohol. Its refractive index is about 1·4800.

Several chemists have investigated this oil, but the only well-defined constituents so far identified are the ketone pulegone, menthol, laevo-limonene, dipentene and menthone. The most valued oil is that obtained from Spanish or Algerian plants, but the oil, although used to a certain extent in pharmacy, is now not extensively employed. A Russian pennyroyal oil is known, which is obtained from a different plant, *Pulegium micranthum*. This oil has a specific gravity of about ·930, and has an odour recalling peppermint and spearmint. The American pennyroyal oil is distilled from a herb indigenous to North America, *Hedeoma pulegoides*. According to Schimmel, the dried leaves yield about 3 per cent., and the leaves and stalks together about 1·5 per cent. of essential oil. The specific gravity varies from 0·925 to 0·940 and the optical rotation + 18° to + 22°. The oil is soluble in two volumes of 70 per cent. alcohol, a characteristic interfered with by the addition of turpentine. The chief ingredient in this oil is pulegone, identical with that from the oil of *Mentha pulegium*. Traces of menthone are also present.

Barrowcliff has recently examined the American oil. The oil used in this investigation possessed the following characters: $d15°/15° = 0·9297$; a_d + 25° 44′ in a 1-dcm. tube; soluble in twice its volume of 70 per cent. alcohol. It was found to consist of: (1) an undetermined phenol, in very small amount; (2) *l*-pinene; (3) *l*-limonene; (4) dipentene, all of these terpenes being present in only small amount; (5) 1-methyl-3-*cyclo*hexanone about 8 per cent.; (6) pulegone, about 30 per cent.; (7) *l*-menthone, and (8) *d*-iso*menthone*, identical with the dextro-rotatory constituent of Beckmann's "inverted menthone"; the amount of these two menthones constituting about 50 per cent. of the oil; (9) a sesquiterpene alcohol, about 2 per cent.; (10) esters of formic, acetic, octoic, decylic and salicylic acids, and the ester of a dibasic acid of

the probable formula $C_8H_{14}O_4$, together with formic, butyric, octoic and decylic acids in the free state; all these esters and acids being present only in small amount.

Mountain Mint Oil is the product of distillation of the herb *Pycnanthemum incanum*, which yields 1 per cent. of an oil of specific gravity about ·910 to ·940, and optical rotation + 3° to + 5°. The oil contains from 7 to 10 per cent. of phenols, chiefly carvacrol, together with some pulegone.

Thyme Oil.—This oil is used to a certain extent for veterinary purposes and cheap soap perfumery, often under the name of *Origanum oil* (which is in reality the product of a species of *Origanum*). The most valued oil is the French distillate, which is the product of *Thymus vulgaris;* a good deal of oil is produced in Spain, but this is at times distilled from an allied species. Two commercial varieties are recognised, the "red" and "white" oils. The former is the crude distillate, and probably owes its red colour to the action of the phenols present on the iron of the crude stills and condensers frequently used. The red oil when properly rectified forms the colourless or "white" oil of commerce. The yield of oil is very variable—sometimes being as low as ·5 per cent., often rising to 1 per cent. in the fresh and 2·5 per cent. in the dried herb. The French oil contains from 20 to 35 per cent. of phenols, chiefly thymol, upon which the value of the oil chiefly depends. The Spanish oil contains often a much higher percentage of phenols (30-50 per cent.) partly carvacrol. As these are sometimes fraudulently removed, it is important that the percentage of phenols should be the basis of valuing the oil. In addition to the phenols, there also occur pinene, cymene, borneol, linalol and bornyl acetate, and probably some terpin hydrate. The genuine oil usually possesses a specific gravity ·905 to ·950 and is slightly laevo-rotary. French oils rarely have a higher specific gravity than 0·935. Its refractive index is about 1·4800 to

1·4950. Admixture with the oil of *Thymus serpyllum* does not alter the specific gravity, but increases the rotation, as this oil rotates up to – 12°. Pure oils are soluble in 1 to 2 parts of 80 per cent. alcohol. Oils adulterated with French turpentine have a high laevo-rotation. A very large amount of the French "white" oil contains a considerable quantity of turpentine. The percentage of phenols is indicated by the decrease in volume on shaking with aqueous solution of potash, and also by the amount of oil distilling above 220°, which should not fall below 25 per cent. Kremers recommends the following method of estimating the thymol:—

Five c.c. of the oil to be examined is weighed and brought into a glass-stoppered burette graduated to $\frac{1}{10}$ c.c., and is diluted with about an equal volume of petroleum ether; a 5 per cent. potassium hydroxide solution is added, and the mixture shaken for a short time, then the liquid is left standing until separation is complete. Then the alkaline solution is allowed to run into a 100 c.c. graduated flask. This operation is repeated until no further decrease in the volume of the oil takes place.

The alkaline solution of thymol is made up to 100 or 200 c.c. as the case may require, using a 5 per cent. soda solution. To 10 c.c. of this solution in a graduated 500 c.c. flask is added a $\frac{1}{10}$ normal iodine solution in slight excess, whereupon the thymol is precipitated as a dark reddish-brown iodine compound. In order to ascertain whether a sufficient quantity of iodine has been added, a few drops are transferred into a test tube and a few drops of dilute hydrochloric acid are added. When enough iodine is present, the brown colour of the solution indicates the presence of iodine, otherwise the liquid appears milky by the separation of thymol. If an excess of iodine is present, the solution is slightly acidified with dilute hydrochloric acid and diluted to 500 c.c. From this, 100 c.c. are filtered off, and the excess of iodine determined by titration with $\frac{1}{10}$ normal solution of sodium thiosulphate.

For calculation, the number of cubic centimetres required is deducted from the number of cubic centimetres of $\frac{1}{10}$ normal iodine solution added and the resultant figure multiplied by 5, which gives the number of cubic centimetres of iodine required by the thymol.

Every cubic centimetre of $\frac{1}{10}$ normal iodine solution equals 0·003741 gramme of thymol. Knowing the quantity of thymol in the alkaline solution, the percentage in the original oil is readily found.

The reaction taking place is represented by the equation :—

$$C_{10}H_{14}O + 4I + 2NaOH = C_{10}H_{12}I_2O + 2NaI + 2H_2O.$$

In the estimation of carvacrol a slight modification of this method must be made, because carvacrol is thrown down as a finely divided white precipitate, giving the solution a milky appearance. In order to form a precipitate the liquid is vigorously shaken after the addition of the iodine solution, and is subsequently filtered. Then the liquid is acidulated with hydrochloric acid, and subsequently the same procedure is followed as was described for thymol. The calculation is also the same. The author, however, is not clear as to what allowance is made for the absorption of iodine by the excess of alkali, and doubts the value of the process.

Labbé has examined an authentic sample of thyme oil (*Bull. Soc. Chim.*, iii., 19, 1009) and found it to contain 30 per cent. of thymol, 17 per cent. of a terpene which he could not identify, 15 per cent. of menthene, 21 per cent. of cymene, 5 per cent. of linalol, 8 per cent. of borneol, and traces of carvacrol.

Thymus capitatus also yields an oil of specific gravity about ·900, and closely resembling the above-described oils. It contains pinene, cymene, dipentene, thymol, carvacrol and bornyl acetate. Its phenol content is about 6 per cent. A similar oil is obtained from *Thymus camphoratus*. A some-

what different oil is obtained from a variety of *Thymus serpyllum* (*citratus* or *citriodorus*). This oil has an odour recalling thyme, lemon and geranium. Its specific gravity is 0·890 to 0·920 and its optical rotation – 10° to – 20°. It contains only a very small amount of phenols.

The value of this oil depends so much upon the phenols it contains that it is important that these should be estimated, as the abstraction of thymol, a valuable commercial product, is by no means uncommon.

Marjoram and Origanum Oils.—Common marjoram oil is the product of distillation of the herb *Origanum vulgare*, sweet marjoram oil being derived from *Origanum majorana*. The Cretic origanum oil is the product of *Origanum hirtum* and *Origanum Smyrnæum*. Sweet marjoram oils have a specific gravity of ·890 to ·910, and are dextro-rotary to the extent of + 5° to + 20°. The oil of *Origanum vulgare* has a specific gravity 0·870 to 0·910 and an optical rotation up to – 35°. Although they resemble oil of thyme, their chemistry has not been completely investigated. The Cretian origanum oil (Spanish hop oil) differs in a marked manner from the marjoram oils. That from *Origanum hirtum* has a specific gravity of ·940 to ·980, and is optically inactive or only slightly laevo-rotary. That from *Origanum Smyrnæum* has a specific gravity ·915 to ·966, and is laevo-rotary from 0 to – 15°. Its refractive index is about 1·5100. The former contains from 60 to 85 per cent. of phenols, chiefly carvacrol, together with some cymene. The latter has been examined by Schimmel & Co. and found to contain from 30 to 60 per cent. of phenols, chiefly carvacrol, together with cymene, and one or more hydrocarbons, probably of the naphthene series, and a large quantity of linalol. A phenol is also present in minute quantity which has not been identified. It is soluble in 3 volumes of 70 per cent. alcohol. The ordinary oil of marjoram is only worth about half as much as "*Ol. Origani Cretic*," which is

used for microscopic purposes. Both are often adulterated with turpentine.

Biltz (*Berichte*, 1899, 995) has recently examined a sample of pure oil of *Origanum majorana*, which had a specific gravity ·898, and a rotation of + 15° 45′. The terpenes (about 40 per cent.) were found to consist chiefly of terpinene. Terpineol and terpenyl esters were also found, the latter chiefly existing as terpinyl acetate (6 per cent.).

Schimmel & Co. have investigated the oil of Cretian origanum, and have found therein cedar camphor. They are not, however, prepared to say that it was a natural constituent or whether it was due to the adulteration of the oil in question.

Patchouli Oil is distilled from the dried leaves of *Pogostemon patchouli*, which yields from 2 to 4 per cent. of oil. This plant is possibly a native of China, but is cultivated to a large extent in the Straits Settlements, Penang, Silhet, Java, Bourbon and Mauritius. There appear to be several varieties, and although one is usually employed for the preparation of the oil, others are not excluded. According to Mr. Fisher (the well-known Singapore distiller), the variety selected for cultivation is known locally as "*Dhelum Wangi*". The green tops of the plant are dried in the shade in large sheds and spread out on bamboo racks, being turned over frequently. It is important that they should not be sun-dried, however. About 25 per cent. of the leaves of the wild plant known as "*Dhelum outan*" are added, as it is said to increase the fragrance of the resulting oil. The distillation is carried out in false-bottom cylinders, with steam at a pressure of about 10 to 15 lb. In Penang two varieties of oil are known, the green and the brown. It has been suggested that the former is obtained from young, and the latter from old leaves, but it is more probable that the differences are due to the influence of soil and climate. Interesting details

as to the cultivation of the plant will be found in Sawyer's *Odorographia* (vol. i., p. 293). Although pure oil distilled in the East is easily obtainable, the fraud practised in certain quarters led to direct importation of the leaves, which are now distilled in Europe. The pure oil has a specific gravity of ·975 to ·995, and an optical rotation of − 50° to − 68°. The refractive index is high, up to 1·512. Its favourite adulterants appear to be cedar-wood oil, cubeb oil, and occasionally turpentine and petroleum. The pure oil should dissolve in an equal volume of 90 per cent. alcohol, the two last-named adulterants interfering greatly with this property.

The earliest chemical examination of this oil was made by Dr. Gladstone in 1864, who stated that it contained a hydrocarbon analogous to that from oil of cubebs, together with a small quantity of an intensely blue colouring matter which he termed cærulein. Gal and Montgolfier have more recently shown that the oil contains a solid body, which they termed patchouli camphor, and which Wallach has shown to be a sesquiterpene alcohol $C_{15}H_{26}O$. This body is probably the oxidation product of other substances in the oil, and appears to have little or no odoriferous value. It is deposited when the oil stands for long in a cold place. When recrystallised it melts at 56°. It is laevo-rotary, about − 100°. Dehydration gives rise to a hydrocarbon $C_{15}H_{24}$ patchoulene. The sesquiterpene occurring naturally in the oil has been shown to be cadinene.

The Imperial Institute Chemical Department have reported on a sample of Perak patchouli oil.

They give the following figures in comparison with samples of ordinary Singapore oil and of German distilled oil:—

	Perak.	*Singapore.*	*German.*
Specific gravity . .	0·9595	0·957 − 0·965	0·970 − 0·995
Optical rotation . .	− 43° 51′	− 44° to − 50°	− 50° to − 60°
Refractive index . .	1·5068	——	——
Solubility in 90 % alcohol	1 : 7·4 vols.	1 : 3 to 7 vols.	1 : 1 vol.

De Jong (*Rev. Trav. chim.*, 24, 309) has made an examination of several varieties of patchouli oil, and gives the following figures:—

	Java Plants.	*Singapore Plants.*	*Java Plants.*
Specific gravity . . .	0·922 at 25°	0·949 at 25°	0·929 at 25°
Optical rotation . . .	− 16° 10′	− 58° 24′	− 42° 18′
Initial boiling point . .	180°	230°	145°
Distils between 250° − 270° .	50 %	60 %	76 %

By the action of sulphuric acid on the oil, the author obtained a sesquiterpene, $C_{15}H_{24}$, boiling at 260° to 263° at 740 mm. pressure. The sesquiterpene from the Singapore oil has a specific gravity 0·915, and optical rotation − 1°, whilst that from the Java oil has a specific gravity 0·897 and optical rotation − 1° 5′. De Jong proposes the name dilemene for (apparently) both these bodies, but does not appear to have shown much evidence of their individuality.

Von Soden and Rojahn (*Berichte*, 1904, 3353) have examined samples of patchouli oil of known purity, and have separated it into two main fractions by distillation under reduced pressure. The earlier fractions of specific gravity 0·984 to 1·002 were found to consist chiefly of patchouli alcohol, whilst two other fractions of specific gravity 0·946 and 0·964 were found to consist of high boiling sesquiterpenes. A series of refractionations succeeded in separating a fraction of specific gravity 0·930 to 0·940 and of optical rotation − 50°, and one of the same specific gravity but of rather higher boiling point. From the former, after hydrolysis, a sesquiterpene was obtained in a state of purity which boiled at 264° to 265° at 750 mm., and had a specific gravity 0·9335 and an optical rotation − 58° 45′. This latter fraction yielded a sesquiterpene of specific gravity 0·930, optical rotation + 0° 45′, and boiling point 273° to 274° at 760 mm.

Simmons has reported (*Chemist and Druggist*, 1904, 815) on some adulterated patchouli oil in which he finds an ester

or esters containing oil obviously added in order to do away with the necessity of using the ordinary crude adulterants, cedar-wood and cubeb oils. He gives the following figures for two samples of the oil in question :—

Specific gravity	0·9948	0·9937
Rotation	−38° 30′	−49° 30′
Refractive index	1·5175	1·5110
Acidity	trace	trace
Ester value	58	18·5
Solubility in 90 % alcohol . .	1 in 0·75	1 in 0·5

The normal ester value of the oil is from 4 to 13.

Schimmel & Co. have found present in this oil not more than 3 per cent. of bodies of any odour value. They found traces of benzaldehyde and eugenol, cinnamic aldehyde and a terpene alcohol. There was also present a ketone yielding a semi-carbazone melting at 134° to 135°. Two bases are present, possessing powerfully narcotic odour. One of them boils at 135° to 140°. It yields a hydrochloride melting at 148°. The base has a refractive index 1·5428, a specific gravity 1·0148, and optical rotation − 9° 5′.

It is to be noted that neither Von Soden nor Schimmel could detect cadinene in this oil, as reported by Wallach.

The fresh leaves of patchouli have been distilled and the oil examined. This was found to have a specific gravity ·943 and optical rotation - 11° 30′. Patchouli oil was once regarded as one of the high-class perfume bases, but its use became a little unpopular, so that it is now more frequently employed in lower-grade perfumery.

Melissa Oil.—This oil, also known as *balm oil*, is distilled from the green herb *Melissa officinalis*. Several species are indigenous to Western Asia and Southern Europe. The leaves possess an odour recalling lemon and citronella (the French *citronelle* is this plant), but the yield of oil is so small, that the melissa oil of commerce is usually obtained by distilling lemon or citronella oil, or a mixture of both,

over the herbs. The genuine oil has been examined by Schimmel & Co., who state that it has a specific gravity from ·890 to ·925, and a rotation of + 0° 30′ to − 6° 30′. It contains citral and probably citronellal. Flatau and Labbé state (*Bull. Soc. Chim.*, 1898, iii., 636) that a specimen they examined contained 20 per cent. of geraniol, 12 per cent. of linalol, and 6 per cent. of citronellol. Its use is entirely confined to perfumery purposes.

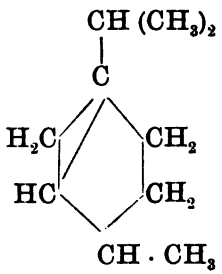
Sage Oil is distilled from the leaves of *Salvia officinalis*, which yield from 1 to 3 per cent. of oil. This is of a pale yellow to greenish-yellow colour and of penetrating odour. Its specific gravity varies from ·910 to ·930, and its rotation from + 10° to + 25°. Its refractive index is about 1·4620; it is soluble in 2 volumes of 80 per cent. alcohol. The known constituents of the oil are the terpene pinene, a sesquiterpene, esters, cineol, borneol and thujone. Muir, working from 1877 to 1880 on this oil, stated that it contained a terpene identical with that from turpentine (pinene), a sesquiterpene which he termed sage-cedrene, a solid "camphor" $C_{10}H_{16}O$, and salviol. which Semmler has shown is identical with thujone. The oil is only employed to a very limited extent.

According to Schimmel & Co. the ester value of this oil is about 100. The author has found great difficulty in obtaining samples of this character, and is of opinion that such oils are rare; 25 is a common ester value for Spanish oils, which may possibly be derived from some different species.

On fractionating German oil of sage H. Seyler obtained 1 to 2 per cent. of a first fraction boiling below 155°, which could be separated into three portions by repeated distillation over sodium. The fraction first passing over, of the boiling point 142° to 145° ($d_{20°} = 0·80$; $n_d = 1·4438$; $a_d = + 1° 40′$), gave analyses corresponding to $C_{10}H_{18}$. This hydrocarbon, called "salvene," when oxidised with potassium permanganate, yielded an acid, whose semicarbazone $C_{10}H_{16}O_2CON_3H_3$

melted at 204°, and which possibly is identical with β-tanacetoketonic acid (β-thujaketonic acid).

Salvene has probably the following constitutional formula:—



From the first runnings of a Spanish oil of sage no salvene could be isolated.

Salvia sclarea also yields an oil with a highly aromatic odour, recalling that of ambergris. It is known commercially as *clary* oil or muscatel sage. The oil has a specific gravity about ·930 and an optical rotation of about − 25°. It probably contains linalyl acetate. Its refractive index is about 1·477. Its ester value is 150. It contains pinene and cineol.

Savory Oil.—The oil distilled from the green herb, winter savory, *Satureja montana*, has been examined by Haller, who states that it is an orange-yellow oil of aromatic taste, somewhat resembling true origanum oil, of specific gravity ·937. He found in it from 30 to 40 per cent. of carvacrol, and traces of another phenol. Two hydrocarbons at least are present, probably cymene and a terpene. A sample examined by Schimmel & Co. had a specific gravity ·939 and optical rotation − 2° 35′. It was soluble in 4·5 volumes of 70 per cent. alcohol, and contained 65 per cent. of phenols. The oil of the summer savory, *Satureja hortensis*, does not differ greatly from that of the winter savory. According to Schimmel, this has a specific gravity ·913 to ·924, and contains carvacrol and cymene. Jahns has examined the oil, but as the sample he

used had a specific gravity ·898 it is probable that it was adulterated with turpentine. He found 30 per cent. of carvacrol in the oil, with traces of a second phenol, cymene, and one or more terpenes. *Satureja thymbra* also yields an oil of specific gravity ·906 which contains pinene, cyenene, dipentene and bornyl acetate.

Sweet Basil Oil.—This oil is distilled from the fresh herb *Ocymum basilicum*, which, according to Schimmel, yields about $\frac{1}{50}$ per cent. of essential oil. Other authorities, however, give as high a yield as 1½ per cent. The former appears to refer to German herbs, whilst the latter refers to the fine Réunion or Java distillate. This oil has a most excellent fragrance, and is used in the preparation of mignonette extract. The German oil has a specific gravity ·900 to ·930, and an optical rotation varying from − 6° to − 20°. Réunion oil, which may be distilled from allied species, has a specific gravity 0·940 to 0·990 and an optical rotation of + 7° to + 12°. It is soluble in 3 to 7 volumes of 80 per cent. alcohol. The old text-books gave "Basil camphor" as its known constituent, which separates in crystals when the oil is kept. Dupont and Guerlain were the first to attempt a thorough examination of this oil. They first examined a French distillate, and found in it methyl-chavicol (*estragol*) and *laevo*-linalol. Schimmel & Co. examined a Réunion oil, and found methyl-chavicol to be the chief constituent of this also. As secondary constituents they found pinene, camphor and cineol. An oil grown at Miltitz, however, contained only 25 per cent. of methyl-chavicol, and differed much in odour from the Réunion oil. This oil contained some cineol, together with an alcohol (probably linalol), but no camphor. Dumas and Péligot some time ago stated that they had discovered a crystalline terpene hydrate in this oil, but neither Dupont and Guerlain nor Messrs. Schimmel & Co. have been able to find this. Traces of a crystalline substance melting at

64° were found in Réunion oil, but in too small quantity to be examined. French and German oils are laevo-rotary, whilst the Réunion distillate is dextro-rotary and has a somewhat more camphoraceous odour than European oils. Further, it contains no linalol. It is a matter of some doubt whether the Réunion plants are *Ocymum basilicum* or some other species.

Several varieties of the oil have been examined in the laboratories at Buitenzorg. One is that from a large-leaved variety known as "Selasih Mekah". The oil had a specific gravity 0·900 at 26° and an optical rotation of − 15° to − 18°. It contained about 30 to 40 per cent. of phenols, of which eugenol is stated to be the principal.

Another variety of the plant yielded an oil of specific gravity 0·948 at 25° and containing much methyl-chavicol. This plant is known as Selasih hidjan.

An olefinic terpene, which has been termed ocimene, was found in these oils, having a specific gravity 0·794 at 22° and refractive index 1·4861. It boils at 73° to 74° at 22 mm. It absorbs oxygen rapidly.

Normal basil oils have a refractive index about 1·4810 and an acid value of about 20 and ester value about 10 to 15.

The following are among the less important oils distilled from plants of the natural order *Labiatæ*. *Hyssop Oil*, from the herb *Hyssopus officinalis*, used to a small extent in perfumery and for the preparation of cordials. Its specific gravity is ·925 to ·940, and optical rotation − 19° to − 23°. The southern regions of the Harz mountains are said to yield the finest material for distillation, but the French and Spanish oils are much esteemed. *Catmint Oil*, from the herb *Nepeta cataria*, specific gravity about 1·040. A Sicilian nepeta oil examined by Umney had a specific gravity 0·927, optical rotation + 12°, total alcohols 22 per cent., and esters 3·3 per cent. as menthyl acetate. *Bugle Weed Oil*, from the

dried herb *Lycopus virginicus*, specific gravity ·924. *Ground Ivy Oil*, from the herb *Glechoma hederacea*, specific gravity ·925. *Dittany Oil* (American), from the herb *Cunila mariana*; this oil has a specific gravity ·915 and probably contains thymol. The total phenol content is about 40 per cent.

N. O. VERBENACEÆ.

Verbena Oil.—Most of the commercial verbena oils and verbena extracts are in reality composed of lemon-grass oil, which has almost entirely superseded the older and true vervain oil. The genuine oil closely resembles lemon-grass oil in general characteristics, but is of more delicate odour. It contains a large quantity of citral, and has a specific gravity about ·900. The plants yielding this oil appear to be *Verbena officinalis* and *Verbena triphylla*. But in Spain a plant known as *Aloysia citriodora* or *Lippia citriodora* yields "verbena oil". This, however, is probably the same plant. The exact character of true verbena oil is somewhat obscure on account of the almost universal use of lemon-grass oil under this name. *Lantana camara*, one of the plants of this natural order, also yields an essential oil. This has a specific gravity ·950 to ·955, and is optically inactive or at most slightly laevo-rotary.

True verbena oil has an optical rotation − 8° to − 16°, but Spanish oil has sometimes a rotation up to + 3° and a specific gravity 0·925. French oil usually contains about 20 to 35 per cent. of citral as against 13 to 20 per cent. in Spanish oil. Kerschbaum has isolated an aldehyde from the Spanish oil which he terms verbenone, $C_{10}H_{16}O$. It has a specific gravity 0·974, refractive index 1·4995, and optical rotation + 66°. Limonene, geraniol, a sesquiterpene and a stearoptene melting at 63° are present in the French oil.

The author and Bennett have recently had the opportunity of examining a small sample of essential oil distilled in the

south of Spain and sent over to this country under the name lemon thyme. The oil is of a yellow colour, and has an odour recalling that of thyme, but with a strong flavour of lemon, differing in this respect from the oil derived from *Thymus serpyllum* (wild thyme) described by Gildemeister and Hoffmann. The latter oil also differs in being laevo-rotatory. The following are the chief characters of the sample we have examined:—

Specific gravity at 15° C.	0·901
Optical rotation in 100-mm. tube	+18° 30′
Aldehydes (principally citral)	20 per cent.
Proportion absorbed by 5 per cent. potash solution	10 per cent.
Refractive index at 19° C.	1·4808
„ „ of first 80 per cent. distilled	1·4779
„ „ of 20 per cent. residue	1·4980

The portion absorbed by potash solution on separation proved to be somewhat resinous, and gave only a feeble phenol reaction with ferric chloride. A small portion of the oil was fractionated in order to give some idea of its possible constituents. The results were as follows:—

Below 175° C.	Nothing distilled		
Between 175° and 180°	10 per cent.	was collected	
„ 180° and 190°	13	„	„
„ 190° and 200°	11	„	„
„ 200° and 210°	12	„	„
„ 210° and 220°	18	„	„
„ 220° and 230°	18	„	„
Above 230°	18	„	residue

These results appear to indicate that pinene is probably absent and that the terpene present is limonene. The high boiling point of the residual fraction, which has a refractive index of about 1·500, points to the presence of a sesquiterpene. The oil is not soluble in 70 per cent. alcohol (10 volumes), but dissolves in 2 volumes of 80 per cent. alcohol.

It is suggested by the distillers that the plant used for distillation is the true vervain, *Lippia citriodora*, but this is open to doubt, as vervain oil has usually a laevo-rotation

and contains a higher percentage of citral. Moreover, it is less soluble. It is, however, rarely found in commerce, and is liable to variation according to the country of origin and method of distillation. The following figures have been published for oil of *Lippia citriodora* :—

	Schimmel.		*Umney.*
Specific gravity . .	0·900	0·902	0·894
Optical rotation . .	− 12° 38′	− 12° 7′	− 16°
Aldehyde (citral) . .	35 %	28 %	74 %

N. O. CONVOLVULACEÆ.

Rosewood Oil.—Rosewood oil or rhodium oil as met with in commerce is almost, if not quite, invariably an artificial mixture of several essential oils in which true oil of roses and oil of geranium or Indian geranium are responsible for the rose or rose-geranium odour. The true oil of rhodium is distilled from the wood, either of the stem or the root, of *Convolvulus scoparius* and *Convolvulus floridus*, two species indigenous to the Canary Islands. It is a thick, viscid, pale yellow oil, darkening on keeping. It has an agreeable rose-like odour and sharp aromatic taste. Its specific gravity varies from about ·900 to ·910. It is laevo-rotary about − 15°. According to Gladstone, it contains 80 per cent. of a terpene; but the authenticity of the sample examined by this chemist is not guaranteed. It is more probable that a large quantity of sesquiterpene is present. According to Schimmel & Co., the oil solidifies at low temperatures to a mass of acicular crystals melting at 11° to 12°. The oil is chiefly used in soap perfumery. The *Bois de rose femelle* is the wood of the so-called Brazilian lign-aloe, and yields the corresponding linaloe oil. It is one of the *Burseraceæ*, and has no connection with the above-described rosewood.

N. O. JASMINEÆ.

Jasmin Oil.—The perfume of the jasmin is one of those which is usually obtained by the process of enfleurage, such

as are those of the tuberose, jonquil, hyacinth, etc. By direct distillation so minute a yield of essential oil is obtained from these plants, that the perfumes are only known in the form of pomades or extracts. The pomade of jasmin flowers, however, yields to suitable solvents, acetone for example, sufficient of the essential oil for thorough examination. The species of this plant are very numerous, but that chiefly used for the preparation of the pomade in the south of France is *Jasminum grandiflorum*, the shoots of which are usually grafted on the stems of the *Jasminum officinale*, which are themselves reared from cuttings. Quite recently some great differences of opinion have been expressed as to the composition of this oil. Verley (*Comptes Rendus*, 30th Jan., 1899) extracted the pomade with acetone and obtained, after evaporation of this solvent *in vacuo*, 40 grammes of oil, which on distillation *in vacuo* left 40 per cent. of resin and yielded 60 per cent. of essential oil. Verley concluded that the oil was approximately composed of 10 per cent. of linalol and 90 per cent. of phenyl-glycol-methylene-acetal ($C_9H_{10}O_2$), which he termed jasmal. These researches led to the granting of a French patent for the production of this body synthetically, as an artificial jasmin oil. The specification states that 50 grammes of phenol-glycol, 30 grammes of sulphuric acid, diluted with 125 grammes of water, and 100 grammes of formic aldehyde are to be heated on a water bath. The resulting body when purified boils at 218°, and is said to have a strong jasmin odour. On the other hand, Hesse and Müller, who have examined a very large number of samples of this oil, state that they have most carefully examined the oil and assert that there is not a trace of this body present, but that the main constituent is benzyl acetate. The following are the figures they give for ten samples of oil prepared by themselves from the pomade:—

No.	Yield per cent.	Specific Gravity.	Rotation.	Esters—calculated as	
				Linalyl acetate.	Benzyl acetate.
				Per cent.	Per cent.
1	·427	1·015	+2° 30′	95·4	73·0
2	·457	1·018	+2° 30′	91·5	70·0
3	·429	1·011	+2° 30′	95·0	72·9
4	·478	1·009	+3° 30′	92·0	70·4
5	·409	1·006	+3° 15′	90·3	69·1
6	·395	1·007	+3° 10′	90·9	70·7
7	·595	1·014	+3° 20′	92·8	71·0
8	·490	1·012	+3° 10′	94·1	72·0
9	·526	1·009	+3° 30′	95·4	73·0
10	·480	1·015	+3° 20′	93·3	71·4

They have made a very careful and exhaustive examination of the oil, and have studied quantitative methods for estimating its components, which led them to the conclusion that the average composition of the oil is as follows:—

	Per cent.
Benzyl acetate	65
Linalyl acetate	7·5
Benzyl alcohol	6
Linalol	16
Other odorous bodies	5·5

(The work of these chemists, which is certainly the most valuable contribution to the chemistry of this oil, may be found in full in the *Berichte*, 1899, pp. 565 and 765.)

Schimmel & Co. could find no jasmal in the oil, and more recently Hesse has found small quantities of indol, methyl anthranilate and a ketone which he terms jasmone, a sweet-smelling oil of specific gravity 0·945 and boiling at 257° to 258°.

There is another compound which can easily be prepared artificially which has a distinct jasmin odour. The styrolene compounds are, as a group, remarkable in that they often possess floral odours. Thus, the *alpha*-substitution products of styrolene $C_6H_5 . CH : CH_2$, such as brom-

styrolene $C_6H_5 . CH : CHBr$, have usually a distinct hyacinth-like odour. Styrolene alcohol $C_6H_5 . CH(OH)CH_2OH$ is identical with phenyl-glycol, the basis of the above-mentioned French patent; whilst *secondary* styrolyl acetate $C_6H_5 . CH(O . CO . CH_3)CH_3$ has itself a marked odour of jasmin. This body can be prepared by the action of bromine on boiling ethyl-benzene. The resulting bromide is heated with silver acetate and glacial acetic acid, yielding styrolyl acetate.

Artificial oil of jasmin compounded on the lines of the above-mentioned facts is now a regular article of commerce. It closely resembles the natural perfume, except that it is less delicate, and is well adapted for high-class toilet perfumery.

N. O. Ericaceæ.

Oil of Wintergreen.—This oil is one of those which is so closely imitated by other oils (*vide Oil of Verbena*) that the commercial article is very seldom the true oil at all. Genuine wintergreen oil is the product of distillation of the leaves of *Gaultheria procumbens*; "commercial" wintergreen oil is almost invariably the product of distillation of the bark of *Betula lenta*, one of the *Betulaceæ* (*q.v.*); or an artificial synthetic oil, methyl salicylate. *Gaultheria procumbens* is a plant of North America, known as the tea berry or partridge berry. The leaves are gathered and distilled in primitive apparatus, either ordinary whisky stills, or stills composed of wooden tubs with copper bottoms. The resulting oil, which is yielded to the extent of ·5 to 1 per cent., has a specific gravity 1·180 to 1·187, and is faintly laevo-rotary (under $-1°$). It distils between 218° to 221°. Its refractive index is about 1·5350. The bark of *Betula lenta*, the sweet birch, yields about the same quantity of an oil of so exactly similar nature that it is now sold as oil of wintergreen to the almost entire exclusion of the true *Gaultheria* oil. In this plant the

oil is the product of decomposition of the glucoside gaultherine. The only physical difference is that it is quite inactive optically, both oils being almost pure methyl salicylate $C_6H_4 . OH . CO_2CH_3$. Cahours (*Liebig's Annalen*, lii., p. 331) was the earliest reliable investigator of wintergreen oil, but his work has been shown to be only partially correct. According to him the oil consisted of about 90 per cent. of methyl salicylate and 10 per cent. of a terpene, which he named gaultheriline. Probably he examined an adulterated oil. Trimble and Schroeter (*Amer. Chem. Jour.*, 1889, p. 398) stated that both oil of wintergreen and oil of birch contained traces of benzoic acid and ethyl alcohol, together with under 0·5 per cent. of a hydrocarbon (different in the two oils). Power and Kleber, however, have examined a very large number of samples, and give as the result of their work the following summary:—

"*Oil of Gaultheria.*—Contains about 99 per cent. of methyl salicylate, together with a small amount of a paraffin, probably triacontane $C_{30}H_{62}$, an aldehyde or ketone, an apparently secondary alcohol $C_8H_{16}O$, and an ester $C_{14}H_{24}O_2$. To the latter body is possibly due the optical activity of the oil, whereas in the oil of birch it may be assumed that this body has suffered inversion through the process of fermentation by which the latter oil is formed.

"A pure fresh oil of gaultheria should show an optical rotation of not less than $-0° 25'$ in a tube of 100 mm.

"*Oil of Sweet Birch.*—This oil consists to the extent of about 99·8 per cent. of methyl salicylate, and, in its unrectified state, contains also a very small amount of the above-mentioned paraffin $C_{30}H_{62}$, and the ester $C_{14}H_{24}O_2$, but does not contain the alcohol $C_8H_{16}O$ which is found in gaultheria oil.

"The oil of sweet birch is always optically inactive.

"Both of these oils have a specific gravity ranging usually

from 1·180 to 1·187 at 15° C. Both of them, as well as the synthetic methyl salicylate, form a perfectly clear solution with five (5) times their volume of 70 per cent. alcohol at about 20° C., which, in connection with other distinctive characters, is an excellent practical test for their purity.

"Neither the oil of gaultheria nor the oil of sweet birch contains any trace of benzoic acid or its esters, nor do either of them contain any terpene or sesquiterpene."

The above facts easily explain the appearance on the market of artificial methyl salicylate, which is easily prepared by a condensation of methyl alcohol and salicylic acid. It has been objected that the odour of the artificial oil is not so fragrant as that of the natural oil, but so long as the salicylic acid used in its manufacture is pure, no exception can be taken to it. As the synthetic oil is worth less than half the value of the natural product of *Betula lenta*, and mixtures of the two are impossible to detect, it is easy to understand how the producing districts in America started importing the *artificial* oil, which returns to commerce as *natural* oil. The purchase of this oil, so far as its origin is concerned, must therefore be largely a matter of trust in the seller. With the exception of the fact that the true oil of *Gaultheria* is faintly laevo-rotary whilst the oil of *Betula* and the synthetic oil are optically inactive, the limits as regards physical and chemical characters are identical for the three oils. The specific gravity should never vary outside the limits 1·180 to 1·187. The oil should give a clear solution with five times its volume of 70 per cent. alcohol. On saponification with alcoholic solution of potash, the oil should give a result equivalent to at least 98 per cent. of methyl salicylate. The salicylic acid resulting from the addition of acid to the saponification product, after a single recrystallisation from alcohol, should melt at 155° to 157°. This will guard

against the use of impure salicylic acid in the preparation of the artificial oil.

This oil is sometimes adulterated with petroleum or light camphor oils, both quite easy of detection; also with sassafras oil, which, in spite of its high specific gravity, is easily detected by its lowering the saponification number, and its characteristic odour remaining after the wintergreen odour has been destroyed by saponification. The oil is used to a certain extent in pharmacy, either as a drug or to cover the nauseous taste of other drugs, but more extensively as a flavouring in the manufacture of such confections as the American chewing gums. Methyl salicylate has been detected in the following amongst other plants:—

BETULACEÆ.	*Discoverer.*	*Year of Discovery.*
Betula lenta L.	Wm. Procter, jr.	1844
Betula lutea Mich. probably, but not yet determined.		
LAURACEÆ.		
Lindera Benzoïn Meissner	Schimmel & Co.	1885
ROSACEÆ.		
Spiræa ulmaria L.	Schneegans & Gerock	1892
ERYTHROXYLACEÆ.		
Erythroxylon coca Lam.	v. Romburgh	1894
Erythroxylon bolivianum (?)	v. Romburgh	1894
POLYGALACEÆ.		
Polygala senega L.	Langbeck	1881
Polygala senega var. latif. Torr. and Gray	L. Reuter	1889
Polygala baldwinii Nuttall	J. Maisch	1890
Polygala variab. H. B. K. *albifl.* D. C.	v. Romburgh	1894
Polygala javana D. C.	v. Romburgh	1894
Polygala oleïfera Heckel	v. Romburgh	1894
Polygala serpyllacea Weihe (*depressa* Warden).	Bourquelot	1894
Polygala calcarea F. Schultz	Bourquelot	1894
Polygala vulgaris L.	Bourquelot	1894
PYROLACEÆ.		
Hypopitys multiflora Scop. (*Monotropa Hypop.* L.).	Bourquelot	1894

TERNSTRŒMIACEÆ.	*Discoverer.*	*Year of Discovery.*
Thea chinensis	Schimmel & Co. .	1897
ERICACEÆ.		
Andromeda Leschenaultii	Broughton . .	——
Gaultheria procumbens L.	Cahours . . .	1848
Gaultheria fragrantissima Wall . .	Broughton . .	1867
(*Gaultheria punctata* Blume . . *Gaultheria Leschenaultii*, D. C.) . *Gaultheria leucocarpa* Blume . . .	Koehler . . .	1879

Numerous other plants are mentioned in Schimmel's *Report*, 1900 (April).

The author has also detected traces of it in some plants of the natural order *Violaceæ*.

Marsh Tea Oil.—Ledum palustre, a plant of this natural order, yields from ½ to 1 per cent. of an essential oil. The plant is one flourishing in marshy places in the northern parts of North America, Asia and Europe. The leaves and flowering twigs are used for distillation, and the oil obtained is of a reddish-yellow colour and sharp taste and odour. The oil appears to consist almost entirely of a sesquiterpene alcohol $C_{15}H_{26}O$, which has been termed ledum camphor, and a sesquiterpene possibly identical with that obtained by treating the camphor with dehydrating agents, and which has been named ledene. Ledum camphor forms long white needles, melting at 104° and boiling at 282°, and is feebly dextro-rotary. The oil possesses strongly narcotic properties, and is said to be occasionally illicitly added to beer to render it more intoxicating. This, however, is very doubtful. The oil from the leaves has a specific gravity of ·925 to ·935, and that from the flowering twigs about ·960.

N. O. VALERIANEÆ.

Valerian Oil.—The ordinary oil of valerian is obtained by the distillation of the root of *Valeriana officinalis*. The Dutch and Thuringian herb was mostly used on the con-

tinent for distillation until the recent introduction of the Japanese root (from the variety *angustifolia*), which yields from 6 to 7 per cent. of oil as against 1 per cent. for the European root. The oils from the two varieties are quite similar, and may be used indiscriminately. That from the European plants has a specific gravity of ·930 to ·960, and an optical rotation of − 8° to − 15°, whilst that from the Japanese variety (known also as Kesso oil) has a specific gravity ·985 to ·995, and is laevo-rotary to about the same extent as the European oil. The acid value is 20 to 50 and the ester value 80 to 100. Its refractive index is 1·4850.

Pierlot investigated this oil some years ago, but his results cannot be accepted in the light of our present knowledge of essential oils. Oliviero has carefully examined some European oils which had abnormally low specific gravities—·875 to ·900, and isolated the terpenes pinene, camphene and limonene; borneol and its formic, acetic and iso-valerianic esters, terpineol, and probably a sesquiterpene, a sesquiterpene alcohol $C_{15}H_{26}O$, and a crystalline bivalent alcohol of the formula $C_{10}H_{20}O_2$, melting at 132°. Bertram and Guildemeister have examined the Kesso oil and found in it the terpenes pinene, camphene and dipentene, terpineol, borneol, bornyl acetate and bornyl iso-valerianate, a sesquiterpene, a blue oil not identified, and kessyl acetate $C_{14}H_{23}O \cdot CO_2CH_3$. This body is the acetic ester of kessyl alcohol $C_{14}H_{24}O_2$, a liquid boiling at 300°, whose chemical relationships are not yet established.

Valerian oil is employed to a considerable extent on the continent as a popular remedy for cholera, in the form of cholera drops, and also to a certain extent in soap perfumery.

Valeriana Celtica, a native of the Swiss Alps and the Tyrol, yields an essential oil with an odour recalling patchouli and chamomiles. Its specific gravity is ·960 to ·970. The yield is about 1 per cent. Messrs. Schimmel & Co. distilled

a parcel of Mexican root which was probably *Valeriana Mexicana*, known locally as *cuittapatti*. The oil had a disagreeable odour of valerianic acid; its specific gravity was ·949, and it was optically inactive. It appears to consist almost entirely of hydrated valerianic acid.

Oil of Spikenard.—This oil, which is the true spikenard or Indian spikenard, has been described as being obtained from various plants, but there now appears to be no doubt that it is obtained from *Nardostachys Jatamansi*, a plant flourishing in the Alpine Himalayas and district. Kemp distilled 56 lb. of the root and obtained 3 oz. of oil, whilst another parcel of 100 lb. yielded 15 oz. It is a pale yellow oil of specific gravity ·975, and optical rotation about – 20°. Although its odour may be considered disagreeable by many, it is highly esteemed in the East as a perfume. Its use is practically replaced in Western countries by that of oil of valerian.

N. O. Compositæ.

This extensive natural order yields a large number of essential oils, but the majority are of small commercial importance.

Chamomile Oil.—There are two varieties of this oil, the Roman chamomile oil, distilled from the flowers of *Anthemis nobilis*, a plant indigenous to the southern and western parts of Europe, and cultivated in Germany, Great Britain, France and Belgium; and the German chamomile oil distilled from the flowers of *Matricaria chamomilla*.

Roman chamomile oil, which is the oil official in the *British Pharmacopœia*, is obtained to the extent of 1 per cent. from the recently dried flowers. When first distilled it is of a blue colour, but usually turns to a greenish or greenish-yellow colour on keeping. It has a characteristic flavour and odour, but not of the nature to justify its use

in perfumery. Its specific gravity varies from ·905 to ·915. Its optical rotation is +1° to + 3°. It is chiefly composed of esters of angelic and tiglic acids, two isomeric acids of the formula $C_5H_8O_2$. The following esters have been identified: isobutyl isobutyrate, isobutyl angelate, amyl angelate, amyl tiglate, hexyl angelate, hexyl tiglate, and possibly esters of an alcohol anthemol, $C_{10}H_{15}OH$. Traces of the free alcohols and acids, probably due to decomposition of the esters during distillation, also exist. Naudin (*Bull. Soc. Chim.*, xli., p. 483) obtained from the flowers, by extraction with light petroleum, two crystalline substances not included in the above list. One of these he terms anthemene, and considers it to be a hydrocarbon $C_{18}H_{36}$ of the ethylene series. It forms microscopic needles melting at 63°.

German chamomile oil from *Matricaria chamomilla* has a specific gravity ·930 to ·940. Its colour is intensely blue, often turning greenish-blue on keeping. It is a thick fluid becoming semi-solid on cooling, commencing to thicken at about 14° and congealing at 1°. It is freely soluble in 90 per cent. alcohol. According to older researches, which are not reliable, the oil consists of chamomillol $C_{10}H_{16}O$, a terpene, and trichamomillol $C_{30}H_{48}O_3$ (the blue portion of the oil). As a matter of fact the only constituents whose identity have been definitely proved are esters of caproic acid, with traces of their decomposition products, together with a solid hydrocarbon or mixture of hydrocarbons, which is probably responsible for the solidification of the oil at low temperatures. This body (or mixture) melts at 53° to 54°, and when perfectly pure is quite white. Messrs. Schimmel & Co. consider it to be a hydrocarbon or hydrocarbons of the paraffin series. Possibly it contains the bodies previously isolated from Roman chamomile oil by Naudin (*vide supra*). The exact nature of the blue constituent of the oil is not known.

Probably it is identical with that existing in wormwood oil.

Halusel has recently shown that free nonylic acid exists in small quantity in the oil. A small amount of stearoptene melting at 24° and consisting of a number of bodies in which esters and alcohols are present were also isolated.

Chamomile oil is often adulterated with cedar and turpentine oils, sometimes with copaiba oil, and, according to some authorities, with milfoil oil. Some of the commercial oil is merely turpentine or lemon oil or a mixture of these oils, distilled over chamomiles. This reprehensible custom of selling low-priced rubbish under unjustifiable names is countenanced by even some reputable firms, who offer in their price lists "chamomile oil" and "chamomile oil with lemon," the latter at about one-fifth of the price of the former.

Feverfew Oil.—The common feverfew, *Pyrethrum parthenium* (*Matricaria parthenium*), yields a small amount of essential oil of strong, characteristic odour. The green flowering herb yields about ·07 to ·4 per cent. of an oil of specific gravity ·900 to ·960. The dried herb yields rather less oil than the fresh plant. Chantard investigated this oil and stated that it contained a terpene and an oxygenated body resembling camphor. In all probability this oxygenated body is a mixture of camphor and borneol. Schimmel & Co. obtained ·068 per cent. of oil from the herbs, which had a specific gravity ·960. Even at the ordinary temperature it contained a considerable number of hexagonal crystals, which appear to be borneol. Bornyl esters are also present, but no camphor could be detected.

Wormwood Oil.—This oil is distilled from the green herb *Artemisia absinthium*, a plant indigenous to the hilly and mountainous regions of Northern Africa, Europe and the north of Asia, and cultivated to a considerable extent in North America. The yield varies from ·2 to ·9 per cent.

The oil is of a greenish or greenish-blue colour, and of characteristic odour and taste. It is frequently known as oil of absinthe. The pure oil has a specific gravity ·925 to ·955. Its refractive index is 1·4600 to 1·4700. It contains a considerable proportion of the ketone thujone. Schimmel & Co. have investigated it, and find a very small quantity of phellandrene and cadinene and the merest traces of pinene present. In addition to these bodies, the oil contains free thujyl alcohol and its acetic, isolvaleric, and palmitic esters. A pure sample examined by means of the acetylation and saponification methods gave results equivalent to 14 per cent. of thujyl alcohol and 15 per cent. of thujyl acetate. The oil is frequently adulterated, the favourite adulterant being turpentine. This is best detected (Schimmel) by distilling 10 per cent. from the oil. This fraction should dissolve to a clear solution in twice its volume of 80 per cent. alcohol. The presence of even a very small amount of turpentine upsets this test. Wormwood oil has a tonic and stimulating effect on the digestive organs, and is sometimes also used externally. It is a constituent of the well-known liqueur, absinthe.

Wormseed Oil.—Ordinary wormseed oil (*Oleum cinæ*) is the product of distillation of the unexpanded flower buds of *Artemisia maritima*, although other species probably contribute to the commercial oil. ("American wormseed" oil is the product of one of the *Chenopodiaceæ*, *q.v.*) The plant is indigenous to the Orient and Southern Russia, Levant wormseed (as the buds are termed) being the most highly valued. The principal constituent of wormseed is the well-known drug santonin, the well-known anthelmintic. The greater part, if not the whole, of the oil found in commerce is obtained from the santonin factories, and is said to differ slightly from the oil distilled from the seeds without extracting the santonin; this, however, is very doubtful. The yield of

oil is about 2 per cent. It is a thick yellow to brownish oil of specific gravity ·915 to ·940. It is slightly laevo-rotary, and is easily rendered colourless by rectification. This oil has been the subject of numerous researches, the results obtained being extr mely variable, no doubt due to difference in the species of *Artemisia* used, or to the employment of adulterated oil. Völckel (*Annalen*, lxxxvii., p. 312) stated that it was a mixture of bodies to which he assigned the names cinæbene and cinæbene camphor, without giving any very definite evidence of their purity. Kraut and Wahlfors (*Annalen*, cxxviii., p. 293) found the chief constituent of the oil to be a substance of the formula $C_{10}H_{18}O$. This body is clearly cineol, which is definitely settled as the principal constituent of the oil. Faust and Homeyer (*Jour. Chem. Soc.*, 1875, p. 371) assigned to the principal constituent the formula $C_{10}H_{16}O$. Hell and Stürcke (*Berichte*, xvii., p. 1970), using the oil from *Artemisia vahliana*, one of the species contributing to the Levant wormseed, confirmed the presence of cineol $C_{10}H_{18}O$. The presence of cineol was again confirmed by Wallach and Brass (*Annalen*, ccxxv., p. 291), who also obtained a terpene from the oil, which is probably dipentene. Another oxygenated body is also present, which may be a compound containing propionic acid, but it has not yet been isolated.

Artemisia Barrelieri yields an essential oil of specific gravity about ·920 which contains thujone. *Artemisia glacialis*, the "mountain wormwood," known commercially as "Genepi des Alpes," yields under ½ per cent. of an oil of specific gravity ·964 to ·970, which solidifies to a buttery consistency at 0°. It has been suggested as a suitable ingredient for making liqueurs to imitate the famous Benedictine and Chartreuse.

Artemisia oil from *Artemisia alba* is an oil of specific gravity 0·9456; optical rotation – 15° 30′; refractive index, 1·4727; and containing 30 per cent. of esters and 25 per cent.

of alcohols. It is soluble in 3 parts of 70 per cent. alcohol and contains laevo-camphene, cineol, camphor and esters of an unknown alcohol. The esters contain some caprylic acid.

Kremers has also examined the following Artemisia oils:—

1. *Artemisia frigida* Willd., submitted in the fresh state to distillation with steam, yielded 0·41 per cent. of a greenish oil with a cineol-like odour; $d_{22°}$ 0·927; a_d − 24° 48′; acid number, 1·2; ester number, 31·8; saponification number, 33·0. The dried herb gave on distillation a yield of only 0·07 per cent. oil of a darker colour; $d_{22°}$ 0·930; acid number, 4·7; ester number, 40; saponification number, 44·7. From the distillation-water of this second distillation, an oil could still be obtained with petroleum ether, which was also darker than the oil from the fresh herb. Rabak states for the extracted oil $d_{22°}$ 0·916; acid number, 5·3; ester number, 25; saponification number, 30·3.

2. From the fresh herb of *Artemisia leudoviciana* Nutt. was obtained 0·38 per cent. greenish-yellow oil with a strong aromatic odour; $d_{22°}$ 0·929; a_d − 16° 14′; acid number, 4; ester number, 10; saponification number, 14.

3. The fresh herb of *Artemisia caudata* Michx. yielded 0·24 per cent. yellow oil with a sweetish odour, which points to the presence of methyl chavicol or anethol; $d_{22°}$ 0·920; a_d − 12° 30′; acid number, 0; ester number, 17·0.

Artemisia vulgaris yields the so-called *mugwort oil*, a liquid of specific gravity ·905 to ·910, containing cineol. *Artemisia abrotanum* is the *southernwood* or *old man* of our gardens, which yields small quantities of a fragrant essential oil. *Estragon oil* or *tarragon oil* is the product of *Artemisia dracunculus*. This plant is a native of Siberia and is cultivated in Europe. The yield of oil from the fresh herb varies from ·1 to ·4 per cent., and from the dried herb from ·2 to·8 per cent. Messrs. Schimmel & Co. have cultivated

this herb at their Miltitz plantations, and give the following figures for three samples of their own distillation:—

	Specific Gravity.	*Rotation.*
1.	·923	+5° 15′
2.	·932	+8° 10′
3.	·906	+5° 45′

The limits may be taken as ·890 to ·960, and for the rotation from + 2° to + 9°. It is soluble in 10 volumes of 80 per cent. alcohol. The odour of this oil, recalling that of anise, led to the statement that anethol was a constituent of the oil. Grimaux and Schimmel are agreed that this is not so, but that the chief constituent is methyl-chavicol (estragol).

This oil is used in the manufacture of various sauces, vinegars and other culinary preparations.

Tansy Oil.—This oil is distilled from the herb *Tanacetum vulgare*, a native of England, but cultivated in France, Germany, the United States, etc. The yield of oil from the fresh herb is about ·1 to ·2 per cent., and from the dried herb about twice this quantity. The specific gravity varies from ·925 to ·950. The rotation of the English oil is about − 25° to − 35°, whilst the American oil is dextro-rotary from + 30° to + 45°. It is soluble in 3 volumes of 70 per cent. alcohol. The earliest thorough examination of this oil was made by Bruylants (*Berichte*, xi., p. 450), who stated that it contained an aldehyde $C_{10}H_{16}O$, which he called tanacetylhydrine. Semmler examined this body and showed that it was a ketone, and renamed it tanacetone. Wallach has shown, however, that it is identical with the ketone of thuja oil which he had already named thujone. Schimmel & Co. showed that the oil contains traces of borneol and some *laevo*-camphor, a fact indicated by Persoz previously (*Comptes Rendus*, xiii., p. 436). The English oil, which is strongly laevo-rotary, also contains much more camphor than the ordinary American oil. A sample distilled by Sawer and

examined by Schimmel & Co. deposited a considerable amount of camphor when cooled to 0°.

The oil is useful for perfuming certain toilet preparations.

Tanacetum balsamita yields about ·07 per cent. of essential oil. According to Schimmel & Co., a sample distilled by themselves had a specific gravity ·943, optical rotation – 53° 48′, and a saponification number equal to 2·1 per cent. of KOH. The limits of specific gravity are about 0·940 to 0·950 and the optical rotation – 40° to – 55°. On standing in a cold place crystals of a paraffin-like substance were deposited. The oil is not soluble in twice its volume of 80 per cent. alcohol, but is in the same quantity of 90 per cent. alcohol. The oil distilled completely between 207° and 283°, and gave the following fractions :—

207°-220° = 10·4 per cent.	240°-250° = 12·4 per cent.
220°-230° = 16·8 ,,	250°-283°= 21·2 ,,
230°-240° = 18 ,,	Residue = 21·2 ,,

Tanacetum boreale yields an oil of specific gravity 0·960 and refractive index 1·4917. Its acid number is about 30; ester number 40, and the oil is soluble in 2 volumes of 80 per cent. alcohol.

Achillea coronopifolia, according to Willdenow, yields an oil of deep blue colour and specific gravity ·924 with a strong odour of tansy. *Achillea moschata* yields the so-called *Iva oil*, of specific gravity ·932. This is a light blue oil containing cineol. *Achillea millefolium* also yields ·07 to ·13 per cent. of oil, the so-called milfoil oil, of specific gravity ·905 to ·925. This also contains cineol, and a very large amount of the blue colouring matter, so characteristic of this series of oils. *Achillea nobilis* and *Achillea ageratum* are also said to be used in the preparation of milfoil oil. That from *Achillea nobilis* is an oil of specific gravity 0·936, optical rotation – 10·4° and containing 18·4 per cent. of

esters and 13 per cent. of alcohols. It contains camphene, borneol, and formic and acetic acids in the form of esters.

Arnica Oil.—Both the flowers and the root of *Arnica montana* yield essential oils, the former to the extent of about ·1 per cent., the latter up to 1 per cent. The plant is indigenous to Europe, growing upon the Swiss and German mountains, and the more northern plains. It is also met with in Northern Asia and the south-western parts of America. The root oil, which is only worth about one-tenth as much as the rarer flower oil, is slightly laevo-rotary, about − 2°, and has a specific gravity from ·990 to 1·000. The chemistry of this oil has been investigated and the following bodies have been identified: phlorone isobutyric ether $C_8H_8(OC_4H_9)_2$, thymohydroquinone dimethyl ether $C_{10}H_{12}(OCH_3)_2$, and phlorone dimethyl ether $C_8H_8(OCH_3)_2$. The flower oil is a blue to bluish-green oil when fresh, turning yellow or brown on keeping. Its specific gravity is ·905 to ·910. When exposed to cold it becomes solid or semi-solid, owing to the presence of a paraffin hydrocarbon. Esters of lauric and palmitic acid are also present. These oils are only used to a small extent in medicine.

Carlina Oil.—This oil is distilled from the root of the thistle, *Carlina acaulis*, indigenous to Central Europe. It is a dark-coloured oil of aromatic taste and odour, of specific gravity from 1·030 to 1·040. This oil has often been examined chemically, but a careful inspection of the figures obtained shows that the results are not reliable.

The oil has been, however, carefully investigated by Gadamer and by Semmler. It contains about 15 per cent. of a monocyclic sesquiterpene, $C_{15}H_{24}$, boiling at 140° at 20 mm., and of specific gravity 0·8733 and refractive index 1·4920. An oxide, termed "Carlina oxide," $C_{13}H_{10}O$, of specific gravity 1·066 and refractive index 1·5860, forms the principal constituent of the oil. It is a complex furane

derivative of the constitution $C_6H_5 . CH : C : CH . (C_4H_3O)$. Semmler has also isolated a sesquiterpene $C_{15}H_{24}$ which he terms carlinene, and a crystalline solid body. Traces of palmitic acid appear to be present.

Costus Oil.—The root of *Aplotaxis Lappa*, a plant indigenous to Eastern India, yields about 1 per cent. of an oil with a characteristic odour recalling that of orris or violets. This plant named as above by Decaisne is identical with *Aplotaxis auriculata* (De Candolle), *Auclandia Costus* (Falconer), and *Saussurea hypoleuca* (Sprengel). It grows at elevations of 7000 to 12,000 feet on the north-western Himalayas, being found freely as far east as Sikkim and as far west as Kashmir and Lahore. The oil is of a light yellow colour, of specific gravity from ·980 to ·987 and optical rotation from + 15° to + 16°. It commences to boil at 275°, and about half distils over below 315°, when decomposition takes place. On keeping, the oil develops an unpleasant odour, which, however, Messrs. Schimmel & Co. claim to remove by a special process which they do not divulge.

Dog Fennel Oil is obtained from the entire plant *Eupatorium fœniculaceum*, which is widely distributed throughout North and South America. The oil has a light yellow colour and a pepper-like odour, not at all resembling true fennel oil. The specific gravity is about ·935 and the rotation about + 18°. It contains a large amount of phellandrene.

Goldenrod Oil.—The oil usually known under this name is that obtained from the "sweet-scented golden rod," *Solidago odora*, a plant very common in the United States east of the Rocky Mountains. Canadian goldenrod oil, however, is yielded by *Solidago canadensis*, of which a sample of authentic origin had a specific gravity ·859 and a rotation − 11° 10′. This is one of the other species closely resembling *Solidago odora*, of which over forty are found

in the United States. The oil contains 85 per cent. of terpenes, as its low specific gravity indicates, which consist chiefly of pinene, together with phellandrene and dipentene, with probably some limonene. Borneol (10 per cent.), bornyl acetate (4 per cent.) and cadinene are also present. *Solidago rugosa* also yields an oil, but it possesses an odour recalling *Origanum* and differs from that above described. The oil from *Solidago odora* has not been thoroughly examined, but it contains much less terpenes than the oil from *Solidago canadensis*.

An oil, believed to be distilled from a mixture of *Solidago odora* and other species, examined by Schimmel, had the following properties: Specific gravity, 0·8904; optical rotation, − 15° 34′; ester number, 34·2; acetyl-ester number, 59·9. The oil contains about 12 per cent. of bornyl acetate.

An oil from *Solidago memoralis* had a specific gravity 0·8799; optical rotation, − 23° 10′; ester number, 14·4, and acetyl-ester number, 38·2.

Fleabane Oil.—This oil, also known as erigeron oil, is distilled from the fresh-flowering herb, *Erigeron canadensis*, a plant widely distributed through North America, and known locally as horseweed, fleabane, butterweed, colt's tail, etc. Only about ½ per cent. of oil is obtained, and this is of a light yellow colour and aromatic odour. The pure oil has a specific gravity of ·850 to ·890, and an optical rotation of about + 65° to + 77°. The known constituents of the oil are the terpene limonene, terpineol and traces of citronellal.

Elecampene Oil is distilled from the root of *Inula helenium*, which yields from 1 to 2 per cent. of oil. The plant is a native of Southern Asia and Siberia, and is found in Southern Europe and North America. According to Marpmann (*Arch. Pharm.*, xxv., p. 826), the oil contains helenin C_6H_8O, alantic anhydride $C_{15}H_{20}O_2$, and alantol $C_{20}H_{32}O$. According to Keallen, the oil consists of a liquid

portion, of the formula $C_{10}H_{16}O$, which he terms alantol, and a solid portion of the formula $C_{15}H_{22}O_2$, which is identical with Marpmann's alantic anhydride. According to Schimmel & Co., helenin is possibly identical with alantic acid, and has the formula $(C_6H_8O)_x$. The probable constituents of the oil are therefore alantic acid, alantic anhydride and alantol, all bodies whose chemical relationships require elucidation.

Helichrysum Oil is the product of distillation of the flowering herb *Helichrysum Stœchas*. It is an oil of specific gravity ·873, and probably contains pinene.

Kiku Oil is distilled from the leaves of *Pyrethrum indicum*. It is a liquid of specific gravity about ·880 to ·890.

Ragweed Oil is a dark green oil distilled from the flowering herb *Ambrosia artemisifolia*, which yields under $\frac{1}{10}$ per cent. of oil. Its specific gravity is ·870, and optical rotation $-26°$.

N. O. Caprifoliaceæ.

Elder Oil is a product seldom seen in commerce. It has been obtained by distilling the fresh flowers with water and extracting the water with petroleum ether. It forms a greenish semi-solid mass with a penetrating odour. According to a very old investigation by Dr. Gladstone, it yields sulphuretted hydrogen when distilled without water, and contains a terpene and a crystalline solid.

POLYPETALÆ.

N. O. Umbelliferæ.

It will be convenient to discuss here two oils yielded by the N. O. *Magnoliaceæ*, on account of their connection with aniseed oil.

Aniseed Oil.—Two varieties of aniseed oil, almost identical in composition and properties, are known in commerce. Of these one is derived from *Pimpinella anisum*, the true

anise, belonging to the natural order *Umbelliferæ*, and the other, which constitutes the bulk of the commercial oil, from *Illicium verum*, the star anise, one of the *Magnoliaceæ*.

Pimpinella anisum is indigenous to Asia Minor and Egypt, and is also cultivated in Russia, Spain, Malta, Greece, Bulgaria, Chili, India and several other parts of Europe. Russia produces the greater part of the anise fruit used for distillation, after which Asia Minor comes chiefly into consideration.

In Russia, from which country most of the fruit used for distillation is obtained, farmers in the districts of Walcysk, Birjutschensk and Ostrog, and to a less extent Podolia, Kursk, Charkow, Tauria and Cherson, cultivate the plant, a portion of the fruit being distilled on the spot, or used for domestic purposes, the remainder being exported. The commercial centres of the anise trade are Krassnaja and Alexejewskaja.

The star anise (*Badiane*) is chiefly found in Southern China and Tonkin. The earliest reliable information as to the actual habitat of this plant was furnished by Mr. Piry in his report on the trade at Pakhoo for the years 1878-79, in which he states that the fruit is brought for export to Kin Chow and Pakhoi from Kwang-Si, chiefly from Lungchow on the borders of Annam, and Po-Sé on the West River close to Yunnan. The oil is chiefly distilled by the natives, and sold to merchants who transfer it to Hong-Kong, where it is bought by the exporters and sent to Europe, sometimes in a grossly adulterated condition. According to Simon, the adulteration is practised not by the distillers, but by the "Bande Noir," as he terms the Chinese merchants who combine to buy the oil from the native distillers, keeping them more or less under their dominion, by means of money advances in the early part of the season. European merchants, however, now have

their agents both in the Kwang-Si and Tonkin districts, who collect the oil immediately it is distilled and transport it either to Hong-Kong, Pakhoi or Haiphong, from where it is shipped to Europe. The greatest care is necessary in purchasing this oil on account of the heavy adulteration, especially with petroleum, practised by the Orientals. In Annam the process of distillation is as follows. About 20 lb. of the fruit are placed in an iron pan and covered with water. Upon this is placed, bottom upwards, so as to form a cover, a second iron pan pierced with a circular opening, over which is placed an earthen vessel with three small orifices in the lower part, which allow the access of vapour into this vessel. These orifices are covered on the inside by small ear-shaped hoods which cause the vapour to be spread over to the sides of the vessel. This earthen vessel is covered with an iron pan, which performs the part of a refrigerator, and into which a continuous current of cold water is admitted. The joints of the first two iron pans are luted and the earthen vessel and the refrigerator are jointed with rag bandages. The vapour reaches the earthen vessel and is condensed when it strikes the bottom of the refrigerator, and falls into a circular trough at the bottom of the vessel, whence it escapes through a small pipe. The average annual production of oil is as follows:—

District of Po-Sé	90,000 kilos.
District of Lung-chow	30,000 ,,
District of Lang-So	30,000 ,,

The yield obtained is from 2·5 to 5 per cent. In Europe the oil distilled from the following growths of *true* anise yielded the following results (Schimmel):—

Chilian . .	1·9 to 2·6	Italian . .	2·7 to 3·5
Macedonian .	2·2	Moravian . .	2·4 to 3·2
Mexican . .	1·9 to 2·1	East Prussian .	2·4
Russian . .	2·4 to 3·2	Spanish . .	3·0
Syrian . .	1·5 to 6·0	Thuringian .	2·4

Aniseed oil is a pale yellow oil of syrupy consistence, solid below about 15°. Its specific gravity is ·978 to ·990, and it is slightly laevo-rotary 0° to −2°, but never dextro-rotary. (Squire has reported some dextro-rotary oils, but they were probably adulterated with fennel oil.) In these, as in other physical properties, no difference of importance exists between the two oils. The pure oil is soluble in 3 volumes of 90 per cent. of alcohol. The refractive index lies between 1·5540 and 1·5600. The *British Pharmacopœia* allows ·975 to ·990 as the limit of specific gravity when taken at 20°—presumably meaning $\frac{d^{20°}}{d^{15°}}$. As it is not easy to keep the oil liquid at 15·5° in certain cases, the gravity may well be taken at the higher temperature. The usual adulterants are petroleum, fennel oil, or its stearoptene, and the waste liquid portion of the oil obtained in the manufacture of anethol (the solid odorous constituent of the oil). In addition, spermaceti has been said to be added, but the author has never met with a sample adulterated with this body. The value of the oil depends on the quantity of anethol it contains, and as this melts at 21° to 22° and boils at 232°, the melting point and the behaviour on fractionation of the oil yield most valuable information as to its purity. With regard to the latter, the fraction obtained between 225° and 235° should not be less than 80 per cent.—usually varying from 80 to 85 per cent.—corresponding to practically that quantity of anethol. Anethol has a great tendency to exist in a state of superfusion, so that the oil can be easily cooled down, if not agitated, below its normal solidifying point, consequently it is necessary either to solidify the oil in a very thin test-tube, and take its melting point, or to determine its solidifying point in Beckmann's apparatus which is illustrated on page 112.

Schimmel & Co. describe the method they adopt in the following terms, and the author considers it yields very concordant results :—

" For the determination of the point of solidification of essential oils, the well-known Beckmann's apparatus for the determination of the molecular weight from the decrease of the freezing point may well be used. A few small modifications make it particularly suited for the examination of anise- and star-anise oils. These slight alterations consist mainly in the removal of the cork-connections, by which the full view of the mercurial column of the thermometer is impeded. The lateral branch of the freezing tube, C, of the Beckmann's apparatus, serving for the introduction of the substance to be examined, can also be omitted. The illustration (see page 112) explains the apparatus as modified by us for our purpose. The battery jar, A, serves for receiving the refrigerating fluid. The test tube, B, suspended in the metal cover serves as aircover around the freezing tube, C, preventing the premature solidification of the oil to be examined. This tube is wider at its top, narrowing down at the junction where it rests on the rim of the lower tube, B. In order to support the tube C in the tube B, three glass protuberances are affixed on its inside about 5 c.c. below its upper rim. The thermometer, divided into $\frac{1}{2}$ degrees, is supported in a metallic cover by three small springs, permitting a ready displacement both upwards and downwards.

" For making the determination for anise- and star-anise oils, the jar is filled with iced water and broken ice, for fennel oil with a freezing mixture consisting of broken ice and common salt. Then the sample of oil to be tested is introduced into the freezing tube, C, reaching to a height of about 5 cm., and the thermometer is inserted into the oil with the precaution not to touch the wall of the tube in any place. During the cooling process any concussions have to be avoided, as they tend to cause a premature solidification of the oil. When the thermometer has reached about 10° below the point of solidification, this being at 6° to 8° for anise- and

star-anise oils, the solidification is induced by gentle friction with the thermometer upon the wall of the tube holding the oil. Should this simple procedure fail in its object, a minute crystal of solidified oil or of anethol may be introduced into the fluid, whereupon the crystallisation sets in at once, disengaging considerable heat. It may be accelerated by constantly stirring with the thermometer, whose mercurial column rapidly rises, soon reaching the maximum height, called the solidification point of the oil."

The solidification point taken in this way, or the melting point, should not be below 15°. It usually varies in pure samples between 15° and 18°, according to the percentage of anethol. A quite satisfactory method of determining the solidifying point is to carefully supercool a small amount in a test tube—say to 10°, add a crystal of anethol and stir with the thermometer, which will now rapidly rise to the correct solidifying point. Small quantities of petroleum do not bring this point below the lowest limit for a pure oil, but even 2 or 3 per cent. greatly interferes with the solubility in alcohol. The pure oil is soluble in three volumes at most of 90 per cent. alcohol, whereas an oil adulterated with 5 per cent. of petroleum will not dissolve in ten volumes. On keeping for any considerable time, the oil becomes partially oxidised, with the formation of anisic aldehyde and anisic acid, with a lowering of the melting point and raising of the specific gravity. A few years ago some samples of aniseed oil appeared on the German and London markets, which possessed an abnormally low melting point. No adulterant could be detected in these, although the melting point varied from 8° to 11°. Two views have been taken on this point. Umney has examined a sample of star-anise leaf oil, which, according to Simon, is largely distilled in the Po-Sé district. He finds its specific gravity to be ·9878, its rotation + 1°, and its solidification point below that of the ordinary fruit oil. A

larger percentage of anisic aldehyde was also indicated by its behaviour on fractionation, and towards the usual aldehydic reagent—fuchsine decolourised by sulphurous acid. Possibly the oil in question was distilled from leaves and fruits. The other view is that the flowers, or very early fruits, are distilled and yield an oil with a much lower anethol content. It is believed that some of the flowers or very young fruits are removed in order to allow the remainder to develop to the best advantage, and instead of being thrown away, these are distilled. Some oil from Tonkin, said to be oil of this description, absolutely free from petroleum and apparently quite authentic, gave the following results :—

Specific gravity	·9916.
Rotation	+0° 23′.
Solidifying point	12°.

A pure commercial oil, however, should certainly solidify not below 15°, should have a specific gravity ·975 to ·990 and an optical rotation 0° to – 2°, and not less than 80 per cent. should distil between 225° and 235°.

Although the physical characters of the true aniseed and the star-aniseed oil are practically identical, the constituents other than anethol, so far identified, are not quite so. Anethol, methyl-chavicol, and traces of anisic aldehyde and anisic acid are so far the only constituents which have been identified with certainty in the oil of *Pimpinella anisum*. Bouchardat and Tardy stated (*Comptes Rendus*, 1896, p. 198) that they found fenchone and anisic ketone $C_{10}H_{12}O_2$ in the oil, but as the sample upon which they worked was dextro-rotary and melted at 10°, it was probably adulterated with fennel oil, and the results are valueless. A further examination showed that the fenchone was due to the presence of fennel oil, but that anise-ketone was present in the oil. It has a specific gravity 1·095. In star-aniseed oil, anethol, methyl-chavicol, anisic aldehyde and anisic acid (in traces), dextro-pinene,

laevo-phellandrene, and the ethyl ether of hydroquinone, and probably safrol, have been detected. Traces of anise-ketone and a laevo-rotary sesquiterpene and possibly a little terpineol are also present. According to Tilden, a dextro-rotary terpene is present in *both* oils.

The leaves of the star anise yield an oil of specific gravity 0·988 or thereabouts, and which is dextro-rotary up to + 1° or + 2°. Its anethol and melting point are low. According to Umney the fruit and leaf oils behave as follows on fractionation :—

	Fruit oil.	*Leaf oil.*
Below 225° . . .	20 per cent.	10 per cent.
226° – 230° . . .	65 ,,	60 ,,
Above 230° . . .	15 ,,	30 ,,

The fruit of a plant, *Seseli Harveyanum*, known in Victoria (Australia) as aniseed, but which more closely resembles fennel, yields an oil which has been examined by Umney, who found its specific gravity to be ·914 and its rotation + 14°. It was still liquid at 4°. The oil thus resembles fennel more than anise oil.

A false aniseed, also belonging to the N. O. *Magnoliaceæ*, is found in Japan under the name "Shikimi no Ki". It is the *Illicium religiosum*, and its oil is known as Shikimi or Japanese star-anise oil. Eijkmann distilled 40 kilos of the leaves—which are usually employed for the preparation of the oil, although the fruit yields an oil—and obtained 177 grammes of oil. It was a strongly refractive, faintly yellow oil of specific gravity 1·006. It contains eugenol, cineol and safrol, and a terpene, probably limonene, with some sesquiterpene. The so-called anise bark oil, prepared by Schimmel & Co. from the bark of *Illicium parviflorum*, which yielded 3½ per cent., is an oil of spicy taste, and odour recalling sassafras and tarragon. It had a specific gravity ·969 and optical rotation – 0° 46′. It consisted chiefly of methyl chavicol, containing very little anethol.

Pure anethol, of melting point 21° to 22°, is now a commercial article, and is preferred by some to the natural oil. The oil is used in perfumery, in the preparation of cordials and liqueurs, and in pharmacy.

Caraway Oil.—This oil is distilled from the seed of *Carum carui*, a plant inhabiting the low-lying lands in many parts of Northern and Central Europe. It is cultivated in England, Germany, Holland, Prussia, Morocco, etc. The Dutch fruit is esteemed very highly, and the oil obtained from it is worth more than that obtained from any other, except English, which however is a matter of local sentiment. Schimmel & Co. give the following as the average yields obtained from various fruits:—

Bavaria, wild	6·5-7 per cent.	German, cultivated	3·5-5 per cent.
Finnish	5-6 ,,	Galician	4·5 ,,
Hessian, wild	6-7 ,,	Dutch, cultivated	4-6·5 ,,
Moravian, cultivated	4 ,,	Norwegian, wild	5-6·5 ,,
East Frisian	5·5-6 ,,	East Prussian, cultivated	5-5·5 ,,
Russian, wild	3·2-3·6 ,,	Swedish, wild	4-6·5 ,,
Styrian	6 ,,	Tyrolese	6·5 ,,
Wurtemburg	5·5-6 ,,		

Caraway oil is one of those whose chemistry is almost fully understood. Normal caraway oil consists almost entirely of two components, the terpene, dextro-limonene, and carvone. There are also present dihydrocarvone, dihydrocarveol and a base not yet identified. Traces of carvacrol may also be present. The physical properties of the two chief constituents are well defined and very different, so that those of the oil give an approximate estimate of the percentage of the two bodies present. They are as follows:—

	Boiling Point.	*Specific Gravity.*	*Rotation.*
Limonene	175°-176°	·846	+ 107° (approx.)
Carvone	224°	·964	+ 62° ,,

Pure caraway oil possesses a specific gravity of ·910 to ·920 (pharmacopœial limits) and an optical rotation of + 70° to + 85°. Samples with a specific gravity below ·910 may

occasionally be found, but in general they should be regarded with suspicion, for if not adulterated, their natural carvone content is low. The refractive index is 1·4870 to 1·4900. The valuable constituent of this oil is the carvone, and on this account, and as it is easy to separate this body in a fairly pure state, carvone is often used in place of the oil, and is official in the *German Pharmacopœia*. The result is that there is much de-carvonised oil on the market to be disposed of. A portion of the carvone is abstracted by fractional distillation, and the misleading name "rectified caraway oil" often given to the remaining oil, which frequently has a specific gravity of ·890 to ·900 and a correspondingly high rotation. When all the carvone is abstracted the resulting "carvene," as it is called—in reality almost pure limonene, with traces of carvone—is sold as "light" oil of caraway. It is used for perfuming cheap soaps, but it is false economy, as the same value in pure oil or in carvol has a far higher odour value, and is cheaper in the end. "Carvene" is comparable to "citrene," the waste terpenes obtained in preparing terpeneless oil of lemons, and "auranciene," the corresponding terpenes from orange oil. They are all practically useless for perfumery purposes, and are either sold under misleading names, or used to adulterate the respective oils from which they have been obtained. There is also an oil known as caraway chaff oil, which appears to be distilled from a mixture of the herb itself, and the chaff obtained on threshing the seeds. "Light" caraway oil examined by the author had a specific gravity ·848 and an optical rotation + 103°. Umney gives a sample of "light" caraway or "chaff" oil as having a specific gravity ·8482 and an optical rotation of – 58·5°. Attempting to determine the question as to when the carvone was formed in the plant, Messrs. Schimmel & Co. distilled the samples described below, grown by them on their Miltitz fields:—

No. 1 from fresh long-cut, blooming plants with partly ripening fruits.

No. 2 from fresh plants cut at the same time and in the same way, from which, however, the umbels bearing both flowers and ripening fruits had been removed, so that the stalks and the leaves alone were distilled.

No. 3 from plants in a more advanced stage of ripening, and after the time of blooming, but before the full ripening of the fruits.

The following were the physical constants of the oils obtained :—

	Specific Gravity.	*Refractive Index.*	*Optical Rotation.*
No. 1	0·882	1·48306	+ 65° 12′
„ 2	about 0·880	1·5083	+ 20° 36′
„ 3	0·9154	1·48825	+ 68° 6′

The odour of oil No. 2 hardly resembled that of caraway seeds, nor did it contain either limonene or carvone, the characteristic constituents of caraway oil, in any perceptible quantity. The small sample was just sufficient for ascertaining the boiling point; it began to boil at 195° C., the thermometer then rapidly rose to 230° C., and between 230° and 270° about 65 to 70 per cent. distilled over; the residue was resinified.

Sample No. 1 evidently contained much more terpene and less carvone than sample No. 3. Hence it is possible that the latter results from the oxidation of the former during the ripening of the plant. A body of high boiling point, not yet identified, was detected in small quantity in each of these oils.

The percentage of carvone being the criterion of the value of this oil, the analysis of it should be especially directed towards this point. A high carvone content is indicated by a high specific gravity and (comparatively) low rotation. These should vary between ·910 and ·920, and + 70° to + 85° respectively. On fractional distillation not

more than 25 per cent. should distil below 185°, and at least 55 per cent. to 65 per cent. should distil over 200°, a considerable fraction—40 per cent. to 50 per cent.—being obtained from 220° to 230°.

Various direct methods of determining the carvone have been proposed, based on the preparation of crystalline compounds of this body (*q.v.*, p. 73). The oxime, the sulphuretted hydrogen compound and the phenylhydrazone have been employed, but only approximate results can be obtained in all these cases. The following are the details recommended in the case of the phenylhydrazone :—

When 5 c.c. phenylhydrazine are added to 5 c.c. of caraway oil the mixture becomes warm owing to chemical combination taking place, and if the action be accelerated by placing the test tube in boiling water for a few minutes a copious crystallisation of carvone phenylhydrazone, $C_{10}H_{14} : N . NH . C_6H_5$, appears, and on cooling the whole solidifies to a crystalline mass. After heating for one hour the reaction is complete, the excess of phenylhydrazine is removed by adding 5 c.c. glacial acetic acid whilst hot, shaking and diluting with 20 c.c. water. The contents of the test tube are then cooled and filtered through a paper disc by means of a pump, and the crystalline mass washed with water until of a pale yellow colour. By this process not only is the excess of phenylhydrazine removed in aqueous solution as acetate, but nearly all the oily terpene adherent to the crystals is washed away. On crystallising from a definite volume of 95 per cent. alcohol the carvone phenylhydrazone is obtained in long silky pale yellow needles, melting at 106° C., but so difficult to dry without decomposition as to render the determination only approximate.

The sodium sulphite process yields good results (see p. 133).

Caraway oil is employed in the preparation of liqueurs, in perfumery and to a certain extent in pharmacy.

Coriander Oil.—This oil is distilled from the fruit of *Coriandrum sativum*, a native of the Levant and Southern Europe, cultivated in many places all over the world. The average yield from various fruits is given by Schimmel & Co. as follows :—

French .	·4 per cent.	Dutch .	·6 per cent.
Italian .	·5 ,,	Moravian .	·8 ,,
Morocco .	·2 to ·3 per cent.	East Indian	·15 to ·2 per cent.
Russian .	·8 to ·1 ,,	Thuringian	·6 to ·8 ,,

Thuringia and Russia have, of late, been the most important producers, the crops from these districts sometimes reaching as high a figure as 450 tons. The oil has an intense odour of the seeds, which is much impaired if immature fruits have been used in the distillation. This is explained by the following experiment undertaken by Schimmel & Co. A portion of a crop was gathered in the early summer, whilst the herb was in early flower, and the whole herb distilled. Five weeks later, when half ripe and just starting to seed, another portion was gathered and distilled. In another month, the fully ripe fruit of a third portion was distilled. The result of the examination of the oils obtained is given below in Messrs. Schimmel & Co.'s own somewhat expressive language :—

"1. *Oil from the entire Flowering Plant in the Green State.*—Yield 0·12 per cent. Sp. gr. 0·853. Insoluble in 70 per cent. alcohol. Extremely objectionable, bug-like odour. After 2½ months the specific gravity of the oil had increased to 0·856. The optical rotation (which had not been determined immediately after distillation) was then + 1° 2′ in a 100 mm. tube at 18° C. The bug-odour had disappeared almost entirely. It would therefore seem that in the meantime the carrier of the odoriferous principle had become polymerised or otherwise transformed.

"2. *Oil from Green Half-ripe Coriander Herb, with Fruit.*

—Yield 0·17 per cent. Sp. gr. 0·866. Optical rotation + 7° 10′ at 18°. Soluble in three parts of 70 per cent. alcohol. Odour resembling that of coriander, with a subsidiary odour reminding of bugs. After one month the specific gravity had increased to 0·869.

"3. *Oil from Ripe Coriander Fruit, distilled immediately after harvesting.*—Yield 0·83 per cent. Sp. gr. 0·876. Optical rotation + 10° 48′ at 16°. Soluble in three parts of 70 per cent. alcohol. Pure coriander odour."

The pure oil has a specific gravity ·870 to ·880, rarely to ·385 (the *B. P.* allows ·870 to ·885). Its optical rotation varies from + 8° to + 14°, rarely falling as low as + 7°. It should dissolve completely in three times its volume of 70 per cent. alcohol. On fractional distillation from 45 to 55 per cent. should be obtained between 190° and 200°, indicating a due proportion of linalol. Its refractive index is about 1·4650 and the ester number from 4 to 23. The most common adulterant of this oil is sweet orange oil, which is detected by the lowering of the specific gravity and the increase in the rotation of the oil. The solubility is also interfered with. Oils of cubebs, cedar and turpentine are also occasionally added.

Semmler (*Berichte*, 1891, p. 206) isolated the characteristic component of this oil, which he termed coriandrol, an alcohol of the formula $C_{10}H_{17}OH$. Barbier has, however, shown that this is identical with *dextro*-linalol (*Comptes Rendus*, 1893, p. 1459). The only other known constituent of the oil is pinene.

Dill Oil is obtained by the distillation of the fruit of *Anethum graveolens*, Linnæus (*Peucedanum graveolens*, Bentham). It is indigenous to Central and Southern Europe, but is found in many other localities, such as the Caucasus, Persia and the north-east of Africa and India. Slight botanical differences exist between the European plant and that grown in India, so that the latter has been described

as a distinct species (*Anethum Sowa*). A difference of opinion exists as to whether this distinction is justifiable, but the oils obtained from the two plants are certainly not identical. The yield of oil obtained from the seeds is about 3 to 4 per cent. The oil (from the European plant) is a pale yellow liquid, of specific gravity about ·905 to ·920 (pharmacopœial limits), although Schimmel & Co. give oils they have distilled themselves with as low a gravity as ·895. This however must be regarded as very exceptional, and a specific gravity below ·905 is generally indicative of the abstraction of carvone. The optical rotation is from + 70° to + 80°. It is soluble in five to eight parts of 80 per cent. alcohol. The refractive index is about 1·4900. In spite of the difference in odour between this and caraway oils, the composition of the two is almost identical, both consisting nearly entirely of limonene and carvone. Dill oil however contains less carvone than caraway oil. Hence the tests given under caraway oil apply here, and stress should be laid on the specific gravity, optical rotation and fractionation. Not more than 15 per cent. should distil below 185°, and not less than 40 per cent. above 220°. English distilled oils usually have the highest specific gravity, from ·910 to ·916, and are consequently held in the highest esteem. The following are the average fractions obtained from English and German oils:—

	English.	*German.*
Below 185° . . .	10 per cent.	10 per cent.
185°-200° . . .	20 ,,	22 ,,
200°-220° . . .	20 ,,	22 ,,
220°-230° . . .	48 ,,	42 ,,
Above 230° . . .	2 ,,	4 ,,

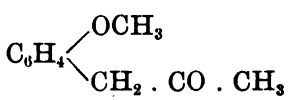
East Indian dill has a much higher specific gravity than European oil, this figure usually varying from ·945 to ·970. Its rotation is from + 40° to + 50°. This high specific gravity is in all probability due to the presence of dill apiol, a body isomeric with ordinary parsley apiol, discovered by Ciamician

and Silber. Indian oil contains much less carvone than European oil, as does the Japanese oil, which also possesses a high specific gravity and appears to be nearly identical with Indian oil. The optical rotation of both varies from + 40° to + 50°. Spanish oil also has a low rotation, from + 50° to + 60° and also contains dill apiol. Schimmel & Co. have found a large amount of phellandrene in a sample of English, and also in Spanish oil. Apart from this, the only known constituents are limonene and carvone, with traces of a solid body, possibly a paraffin hydrocarbon, and, in Indian oil, dill apiol $C_{12}H_{14}O_4$. Pure dill oil is used to a considerable extent in pharmacy as a carminative.

Fennel Oil.—This oil is distilled from the fruit of several varieties of *Foeniculum vulgare*, which is found all over Europe except in the north and north-east, being especially common on the Mediterranean littoral, and is also found in Asia Minor, Persia, India and Japan. Two oils are recognised in commerce, the "sweet" and "bitter" oils, the former being more esteemed. The sweet fennel is said to be *Foeniculum sativum*, but this is probably only a variety of the common wild fennel. The yield of oil obtained is very variable, according to the fruit distilled. In general it averages from 2·5 to 4 per cent. In the ordinary way, Galicia and Roumania furnish some of the best fennel crops, and from their fruit a large portion of the oil of commerce is distilled. The great variability in the fruits of different districts makes it necessary to fix some limits for the physical characters of the oil, which, however, may be exceeded in individual cases. The terpenes, pinene, phellandrene, dipentene and limonene, have all been detected in bitter fennel oils, and the ketone fenchone, and anethol. All these bodies, however, may not occur in any given sample. Upon the presence of anethol the value of the oil chiefly depends, and the solidifying point of the oil is therefore a fair criterion

of its value, if the oil is pure. A good oil will contain as much as 60 per cent. of anethol. The specific gravity should not fall below ·960 nor above ·980, and the optical rotation should vary from + 10° to + 25°. The solidifying point (see *Oil of Aniseed*) should not fall below + 3°. If necessary the crystalline stearoptene may be separated and examined, but as a rule added solid bodies will alter the other characters of the oil. The oil is soluble in an equal volume of 90 per cent. alcohol. The refractive index is from 1·5250 to 1·5350. The above tests will guard against the abstraction of anethol, or the addition of the residue of oil from which this body has been abstracted.

One observer gives as the specific gravity and optical rotation of the oil distilled from French bitter fennel, ·910 to ·955 and + 22° to + 48° respectively. Tardy, however (*Bull. Soc. Chim.*, xvii., p. 660), has examined a sample of this oil, and states that its specific gravity is 1·007 at 0°, and its optical rotation + 18° 20′. In the oil he found pinene, dipentene, cymene, phellandrene (?), *d*-fenchone, methyl-chavicol and anethol, together with anise aldehyde and anisic acid, and a ketone of the constitution—



Schimmel & Co. have examined a sample of Japanese oil, and give the specific gravity as ·9754, and the optical rotation as + 10° 3′. Umney gives ·9754 and + 15° 5′ for a sample of the same oil. He found 10·2 per cent. of fenchone in the oil.

Foeniculum piperitum yields an oil (*Sicilian fennel oil*) of specific gravity about ·950. Water fennel oil is obtained from the plant *Phellandrium aquaticum* (*Oenanthe phellandrium*), the fruit of which yields from 1 to 2 per cent. of oil of specific gravity ·860 to ·890. The chief constituent of the

oil is the terpene phellandrene, but other constituents are certainly present, although not yet identified.

The sweet Roman fennel, as it is termed, usually contains much anethol and little or no fenchone. It has an optical rotation of about + 7° to + 17°, and melts at 10° to 12°. Macedonian fennel yields a very similar oil. Wild bitter fennel, growing in France, Spain and Algeria, yields an oil of specific gravity 0·905 to 0·925 and an optical rotation up to + 50°. It is practically free from anethol. Indian fennel oil has a specific gravity ·970 and an optical rotation + 21°.

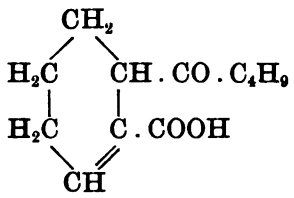
Tardy has examined an Algerian oil of specific gravity 0·991 and optical rotation + 62°. He found present: pinene, phellandrene, fenchone, methyl-chavicol, anethol, a sesquiterpene and a little thymohydroquinone. Schimmel & Co. find camphene in fennel oil, but are not able to confirm the presence of cymene. Traces of basic compounds were also detected.

Cumin Oil or *Cummin Oil* is obtained from the fruit of *Cuminum cyminum*, a native of Upper Egypt and Ethiopia, but cultivated in Arabia, India, China, Malta, Sicily, etc. The bulk of the supply of commerce is obtained from Sicily, Malta, Mogador and India. The yield is from 2·5 per cent. to 4 per cent. of a light yellow oil of specific gravity ·890 to ·930 and optical rotation + 4° to + 8°. Distillates of high gravity dissolve in 3 volumes of 80 per cent. alcohol, but low gravity oils require 8 to 10 volumes. The known constituents of this oil are cymene and cumic aldehyde and a terpene not yet identified. Wolpian (*Pharm. Zeit. für Russland*, 1896, p. 97) states that he has obtained from cumin oil a fraction boiling at 157° to 158°, which was a terpene which he could not identify with any known terpene. However, it is doubtful whether he obtained it in a state of purity, and the proposed name hydrocuminene appears rather premature, as no derivatives were prepared. The oil is not used very extensively.

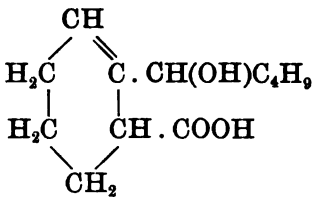
Oil of Lovage.—The ordinary oil of lovage is obtained by distilling the roots of *Levisticum officinale* with steam, the yield being under 1 per cent. The oil is a somewhat dark brown viscous liquid of specific gravity 1·005 to 1·045, and optical rotation from + 2° to + 7°. It is soluble in 3 volumes of 80 per cent. alcohol. Braun (*Arch. Pharm.*, 1897, iii., p. 1) has investigated it, but he did not succeed in characterising any single constituent of the oil. Schimmel & Co. have detected terpineol in it, but, so far, the other constituents are unknown. The fresh herb also yields from ·1 to ·2 per cent. of an oil of specific gravity ·905 to ·940 and optical rotation + 15° to + 45°. The fruit yields 1 to 2 per cent. of an oil of specific gravity ·930 to ·940. Lovage oil is chiefly employed in liqueur and cordial making.

Celery Oil.—All parts of the herb *Apium graveolens*, the common celery, yield essential oils, of which that from the seeds is most valued. Schimmel & Co., however, state that that from the green leaves most exactly reproduces the natural celery flavour. The oil from the seed is obtained to the extent of about 3 per cent., as a liquid of strong celery odour, having a specific gravity ·870 to ·895 and an optical rotation + 65° to + 80°. The chief constituent of the oil is dextrolimonene. Ciamician and Silber have recently (*Berichte*, 1897, p. 492) examined the high boiling fractions of the oil and found therein traces of palmitic acid, guaiacol and a crystalline substance of the formula $C_{16}H_{20}O_3$, melting at 66° to 67°. In addition, a sesquiterpene was found, and two bodies, both acids, of a peculiar constitution, sedanolic and sedanonic acids, together with the lactone of the former, sedanolide, which appears to be the chief odorous constituent of the oil. Sedanolic acid $C_{12}H_{20}O_3$ is a crystalline body melting at 88° to 89°, and is easily converted into its lactone sedanolide $C_{12}H_{18}O_2$. Sedanonic acid $C_{12}H_{18}O_3$ melts at 113°, and possibly occurs as an anhydride in the oil. These two acids

are nearly related, and Ciamician and Silber consider that sedanolic acid is *ortho*-oxyamyl-tetrahydrobenzoic acid, and that sedanonic acid is a related ketonic acid. The following formulæ thus express the relations of these bodies:—

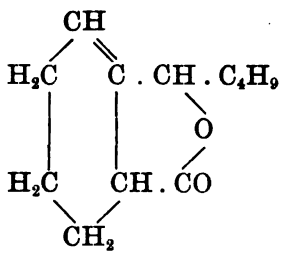


Sedanonic Acid.



Sedanolic Acid.

Sedanolide, the chief odorous constituent, would thus be tetrahydrobutyl-phthalide of the formula—



A closely related body, phthalylisopropylidene, and its reduction products, were prepared artificially and found to have an odour much resembling celery.

The green herb yields ·1 per cent. of an oil of specific gravity ·848 to ·855 and optical rotation + 45° to + 55°. Although it has not been thoroughly examined, it is probable that its constituents closely resemble those of the seed oil. The oil is soluble in ten parts of 90 per cent. alcohol.

Parsley Oil.—All parts of the common parsley, *Petroselinum sativum*, yield an essential oil, of which that from the green herb itself is most esteemed, although that from the seed is the commoner oil. The yield from the seeds is from 2 to 6 per cent. of an oil of specific gravity 1·050 to 1·100. It is *laevo*-rotary about − 5° to − 10°. The two well-ascertained

constituents are pinene and apiol. If the oil contains more than a certain quantity of the latter body it is semi-solid at ordinary temperatures, whilst in any case crystals are deposited on exposure to cold. German oil is rich in apiol, but French oil contains very little. Apiol is prepared from the oil either as a thick liquid, or in the purer crystalline condition, and is used to some extent in medicine.

The oils from the fresh herb and root resemble that from the seed, but are usually *dextro*-rotary. Further, the herb oil has a specific gravity as low as ·925 and has a slight dextro-rotation.

Mourgnes has isolated a body of the formula $C_{14}H_{18}O$ from parsley oil, which he has named cariol. It appears to be closely related to myristicin. Thoms has isolated pinene, myristicin and isomyristicin from a French oil of parsley.

Ajowan oil is the product of distillation of the fruit of the herb *Ptychotis Ajowan* (*Carum Ajowan*), a plant cultivated in many parts of Egypt, Persia, Afghanistan and Bengal. The fruit yields from 3 to 4 per cent. of oil of specific gravity ·900 to ·930, with a slight dextro-rotation. The characteristic odour of the oil is due to the presence of from 40 to 50 per cent. of thymol. In addition, cymene and probably a terpene are present. The oil itself is used to a certain extent in India for medicinal purposes, but its principal use is for the preparation of thymol. According to Stohmann, carvacrol is also present, but this statement requires confirmation.

Angelica Oil.—All parts of the herb *Angelica officinalis* (*Angelica Archangelica*) yield essential oils, of which the best known is that distilled from the fresh root. The plant is a native of Europe, on mountains [illegible] sides, especially in Lapland, Sweden, Norway, Ge[illegible] It is culti[illegible] to a considerable extent in Saxo[illegible] mparatively in Britain. Although the roo[illegible] nostly u[illegible] held in high esteem, accordin[illegible] l & C[illegible]

oil is preferable to this. Angelica root oil is a light yellow or reddish limpid liquid of strong aromatic odour and pungent taste. The yield from roots grown in the Saxon Erzgebirge is about 1 per cent. of oil. The specific gravity varies from ·854 to ·918, that from the dried root usually having a higher specific gravity than that from the fresh root. The optical rotation varies from + 18° to + 36°, usually about + 25°. The refractive index is about 1·4800. On long standing crystals are deposited, which according to Giordani have the composition $C_{32}H_{62}O_5$, and melt at 74° to 77°. Beilstein (*Berichte*, 1882, p. 1741) showed that the oil contains one or more terpenes; Naudin (*Berichte*, 1883, p. 1382) confirmed this, and Schimmel & Co. have showed that amongst the lower boiling fractions of the oil, dextro-phellandrene exists. Ciamician and Silber (*Berichte*, 1896, p. 1811) showed that the crystalline bodies (of which they separated two) existing in the oil were probably oxyacid anhydrides. Hydrocarbons, probably sesquiterpenes, were also found, which distilled at 240° to 270°, and oxypentadecylic acid $C_{15}H_{30}O_3$. Giordani also isolated methyl-ethyl-acetic acid from the oil. The oil obtained from the seeds, which yields about 1 per cent., has a specific gravity ·856 to ·890, and an optical rotation of + 10° to + 13°. It contains phellandrene, methyl-ethyl-acetic and oxymyristic acids. The oil distilled from the whole fresh herb has a specific gravity ·869 to ·890, and an optical rotation + 8° to + 25°. Japanese angelica root, from which an oil is distilled, is from *Angelica anomala* (*Angelica refracta* ?). The oil, which is obtained to the extent of ·1 to ·2 per cent. of the root used, has a specific gravity ·910 to ·915. At 10° it becomes thick, and at 0° it solidifies to a paste. The crystalline mass thus deposited consists mainly of a fatty acid melting at 62° to 63°. The oil distils over between 170° and 310°; the last fractions have a blue-green colour. This oil has a more acrid odour than the Saxon oil, but distinctly

recalls musk, although this is to a great extent covered by the other and less pleasant odour of the oil. The chief employment for angelica oil is in liqueur making.

Carrot Oil.—The seed of the carrot, *Daucus carota*, yields from 1 to 1·5 per cent. of oil of specific gravity ·870 to ·930 and optical rotation − 13° to − 40°. The oil has a characteristic carrot odour and contains pinene and either terpineol or cineol, possibly a mixture of both. The characteristic body responsible for the odour of this oil has not yet been identified.

Ammoniacum Oil is the oil obtained by distilling the gum resin of *Dorema ammoniacum* with water. The yield of oil is very small, usually about ·3 per cent. The oil has a specific gravity of about ·890, and is slightly dextro-rotary. It distils between 250° and 290°. Its composition is not known.

Asafoetida Oil.—The gum resin of certain species of *Ferula*, chiefly, in all probability, *Ferula Narthex* and *Ferula scorodosma*, both perennial herbs, indigenous to Turkestan, Bokhara, Western Afghanistan and Cashmir, yields, when distilled with water, about 3 to 4 per cent. of a somewhat foul-smelling oil of specific gravity ·975 to ·990 and optical rotation about − 10°. Semmler has investigated this oil, having separated by fractional distillation under reduced pressure two terpenes, one of which was probably pinene, and a sesquiterpene, which had a lavender-like odour. The remainder of the oil consists chiefly of compounds containing sulphur. According to Brannt, the oil contains allyl sulphide and allyl disulphide, but Semmler denies this. Sulphur compounds of the formulæ $C_7H_{14}S_2$, $C_{10}H_{20}S_2$, $C_8H_{16}S_2$ and $C_{10}H_{18}S_2$ were found, together with an oxygenated body of the formula $C_{10}H_{16}O$, or a multiple of this.

Galbanum Oil is the product of distillation of the gum-resin *Peucedanum galbaniflorum* and probably other species indigenous to Persia. From 12 to 24 per cent. of oil is obtained, which has a penetrating odour and sharp taste.

Its specific gravity is ·910 to ·940, and its optical rotation from − 5° to + 20°. The only constituents yet identified are pinene and cadinene.

Opoponax Oil.—The oil distilled from opoponax resin, as used in perfumery to-day, is *not* the product of the umbelliferous plant *Opoponax Chironium*. It will be noticed later.

Heracleum Oil.—The ordinary heracleum oil is distilled from the fruit of *Heracleum sphondylium*, the cow parsnip. The yield is from 1 to 3 per cent. of an oil of specific gravity about ·860 to ·880, and slightly *dextro*-rotary. According to Zincke, it contains octyl alcohol $C_8H_{17}OH$ and its acetic ester $C_{10}H\ O_2$ and caproic ester $C_{14}H_{28}O_2$. According to Möslinger, ethyl butyrate is also present; and also the lauric acid ester of octyl alcohol, and some hexyl compounds in very small quantities. The oil of *Heracleum giganteum* has been examined by Gutzeit, and found to correspond closely with that just described. Schimmel & Co. give the following interesting details of this oil:—

It is now well known that this oil is obtained from the fruit or the entire umbellate heads of *Heracleum sphondylium* L. A distillate which we have obtained from the dry umbels from which the fruit had been removed, is for this reason interesting. The yield of oil amounted to 0·08 per cent. The odour of the brownish yellow oil differs distinctly from that of the fruit. $d_{15°}$ 0·9273; α_d − 0° 48′; acid no. 16·2; ester no. 148·6; ester no. after acetylation 195·9; soluble in 1·1 vol. 80 per cent. alcohol; when more solvent is added opalescence and strong separation of paraffin occur. For comparison we give below the properties of two oils distilled from the fruit only.

1. Yield (compared with dry material) 0·9 per cent.; $d_{15°}$ 0·8744; α_d + 0° 38′; acid no. 15·9; ester no. 215·4; ester no. after acetylation 285·3; soluble in 0·8 and more vol. 80 per cent. alcohol; not entirely soluble in 70 per cent. alcohol.

2. Yield (compared with dry material) 1·21 per cent.; $d_{15°}$ 0·8798; a_d + 1° 6′; acid no. 7·3; ester no. 242·4; ester no. after acetylation 276·3; soluble in 1 and more vol. 80 per cent. alcohol.

A distillate from the dry, ripe fruit of *Heracleum giganteum* L. (yield 3·6 per cent.) behaved as follows: $d_{15°}$ 0·8722; a_d + 1° 14′; acid no. 1·6; ester no. 288·3; ester no. after acetylation 314·2; soluble in 1 and more vol. 80 per cent. alcohol. The colourless oil had a peculiar odour, similar to that of common heracleum oil.

Masterwort Oil is distilled from the root of *Imperatoria ostruthium*, a plant indigenous to the mountain regions of Southern and Central Europe. The root yields about 1 per cent. of oil of characteristic aromatic odour, which, according to Hirzel, contains bodies resembling terpene alcohols. Wagner states that angelic aldehyde is present. The oil has a specific gravity about ·875, and distils almost entirely between 170° and 190°

Mew Oil is obtained from the root of *Meum athamanticum* to the extent of about ¾ per cent. The oil has a specific gravity of just over 1·000, and distils between 170° and 300°.

Sumbul Oil or *Musk-root Oil* is obtained from the dried root of *Ferula sumbul*. The yield of oil is only from ·2 to ·4 per cent. Its specific gravity is ·950 to ·965. It has a distinct musk-like odour, and in India the root of *Dorema ammoniacum* is often substituted for it and used under the name of sumbul root (see ammoniacum oil).

Pastinac Oil is obtained from the fruit of *Pastinaca sativa*. The yield is 1·5 to 2·5 per cent. of an oil of specific gravity ·870 to ·890, with a faint laevo-rotation. It somewhat resembles heracleum oil, containing ethyl alcohol, and propionic and butyric acid esters of octyl alcohol.

Haensel has recently shown that heptylic acid is a normal constituent of the oil.

Schimmel & Co. have distilled pastinac oil, for the first time from cultivated plants (*Pastinaca sativa* L.) from the irrigated fields at Miltitz. They submitted separately to distillation with water vapour, the ripe dried seeds, the umbels, and the roots of the plants.

1. Oil from dry seed of *Pastinaca sativa* L.—The bright yellow oil obtained in a yield of 1·47 per cent. had the following properties: $d_{15°}$ 0·8736; a_d – 0° 9′; $n_{d20°}$ 1·43007; acid no. 4·4; ester no. 240·6; ester no. after acetylation 276; soluble in 2½ and more vol. 80 per cent. alcohol.

2. Oil from dry umbels of *Pastinaca sativa* L.—The oil had a dark brown colour, and had a very remote odour of oil of ambrette seeds. It was obtained in a yield of 0·3 per cent.; $d_{15°}$ 1·0168; a_d – 0° 50′; $n_{d20°}$ 1·50049; acid no. 4·2; ester no. 62·9; ester no. after acetylation 86·2; soluble in 6·5 vol. 80 per cent. alcohol, with separation of paraffin.

3. Oil from the dry roots of *Pastinaca sativa* L.—The bright yellowish oil, which in odour reminded somewhat of vetiver oil, was obtained in a yield of 0·35 per cent., and had the following properties: $d_{15°}$ 1·0765; a_d – 0° 10′; $n_{d20°}$ 1·52502; acid no. 3·9; ester no. 12·6; ester no. after acetylation 33·7; not completely soluble in 10 vol. 80 per cent. alcohol; soluble in 0·6 and more vol. 90 per cent. alcohol.

Peucedanum Oil.—The root of *Peucedanum officinale* and the fruit of *Peucedanum grande* yield small quantities of oil, both of specific gravity about ·900 and optical rotation + 30° to + 35° or thereabouts.

Pimpinella Oil is obtained from the dried root of *Pimpinella saxifraga*. Its specific gravity is ·960. It has an agreeable parsley-like odour, and commences to boil at about 240°. Its constituents are not known.

Silaus Oil is the product of distillation of the fruit of *Silaus pratensis*. The yield is 1 to 1·5 per cent. of a slightly dextro-rotary oil of specific gravity ·980 to ·990.

N. O. Myrtaceæ.

Pimento Oil or *Allspice Oil* is distilled from the fruit of *Pimenta officinalis*, Linn. (*Eugenia pimenta*, De Candolle.) The plant, a handsome evergreen, is indigenous to the West Indies, being found especially on calcareous soil near the coast on the islands of Cuba, Hayti, Trinidad, Domingo, Antigua, the Leeward and Windward Islands, and in abundance in Jamaica. The berries are gathered in an unripe condition, as when ripe they are filled with a sweet pulp lacking the characteristic aroma of the green berry. These unripe berries, dried in the sun, form the pimento of commerce, and Jamaica alone exports, chiefly from the port of Kingston, about £50,000 worth per annum. The fruit, which is about the size of a small pea or large peppercorn, has an aromatic odour somewhat recalling cinnamon, nutmeg and pepper, with a predominating odour of cloves. This explains the origin of the name allspice. It yields from 3 to 4½ per cent. of oil on distillation, of a dark reddish colour and of the same aromatic odour as the fruit. So far the well-ascertained constituents are the phenol eugenol with small quantities of cineol, laevo-phellandrene, caryophyllene, eugenol methyl ether and palmitic acid. The eugenol is, of course, responsible for the clove-like odour of the oil, and the other bodies, together with one or more as yet unknown constituents, modify the characteristic odour of the oil. A certain amount of resin, due no doubt to the unstable nature of some of the constituents, is usually present. The actual amount of eugenol in the oil is best estimated by Thom's process (see *Oil of Cloves*), and the remarks made in the monograph on oil of cloves on this estimation, apply here. The specific gravity of the oil is, to an extent, an indication of the amount of eugenol present, and should vary between 1·025 and 1·055. The *British Pharmacopœia*, in which this

oil is official, states that the specific gravity should not fall below 1·040. The oil is laevo-rotary, but never exceeds – 4°, usually about – 2°. It is easily soluble in 90 per cent. alcohol and in twice its volume of 70 per cent. alcohol. Eugenol boils at 247°, consequently the fraction 245° to 250° should be considerable—in genuine oils not below 60 per cent., usually 70 per cent. or over. The amount of eugenol, as estimated by Thom's process (see *Oil of Cloves*), should not be less than 65 per cent.; and the residue not absorbed by caustic potash solution should not exceed 25 per cent.

Pimento leaves yield an oil of specific gravity 0·889 and optical rotation – 1°. It contains citral.

This oil is used almost entirely as a flavouring agent, and it may be noted that the odour of the pure oil imported into this country is quite as fine, if not finer, than that distilled here.

Oil of Cloves.—The clove tree is a beautiful evergreen, indigenous to the Molucca Islands. It is cultivated in several of the islands to the south of the Moluccas, and in Sumatra, Penang, Malacca, Madagascar, the Seychelles, Bourbon, Mauritius, the West Indies, Zanzibar, and Pemba, our chief supply coming from the two last-named islands. The tree is *Eugenia caryophyllata* (*Caryophyllus aromaticus*, Linn.), and most parts of the tree have a very aromatic odour. The spice we know as cloves consists of the dried unexpanded flower buds, which are used in the distillation of the oil. The flower stems are also used, but the oil, although of very similar character, is not of so fine an aroma. As a spice Penang cloves fetch the highest price, but Zanzibar cloves are highly esteemed in commerce; it must be remembered, however, that the majority of "Zanzibar" cloves in reality come from the adjacent island of Pemba. A sophistication sometimes practised on this article is the addition to the natural clove of spent cloves from which the oil has been

distilled, the latter of course being quite valueless as a spice. Few plants yield so much essential oil as does the clove. Genuine buds seldom yield under 15 per cent., often as much as 18 or 19 per cent. The flower stems, however, only yield about 6 per cent.

The most important constituent in oil of cloves is the phenol eugenol, upon the amount of which the oil is regularly valued. It is present to the extent of from 80 to over 90 per cent. In addition to this body the sesquiterpene caryophyllene, esters of eugenol, methyl alcohol, furfurol and traces of an aldehyde not yet identified have been found in this oil. Heine states that traces of naphthaline are also present. This has been confirmed by the author. Traces of salicylic acid are present, probably in the form of eugenol ester. Amyl-methyl-ketone is present in very small amount, and probably traces of methyl benzoate. Traces of caryophyllin ($C_{10}H_{16}O_4$) are probably also present (*Monats. für Chemie*, 1905, 379). Pure clove oil has high refractive index, never falling below 1·5280, and usually reaching 1·5320.

The high specific gravity is indicative of the high eugenol content, but the presence of the bodies above mentioned does not allow of the percentage of eugenol being exactly proportional to the specific gravity, as it would be if no other body but caryophyllene were present. The approximate proportions of the two chief constituents however may be judged by the fact that pure caryophyllene has a specific gravity of about ·908, whilst that of eugenol is 1·070. Pure clove oil (from buds) has a specific gravity, according to the *British Pharmacopœia*, of at least 1·050. The author has found a slightly lower gravity in an absolutely pure sample drawn by one of the most reputable drawers in England. 1·048 to 1·065 will be found to cover all genuine samples, except those, of course, which are specially rectified to ensure a higher eugenol content, when the specific gravity approaches

1·070. Occasionally, especially in an oil distilled from amboyna cloves, the specific gravity will fall to 1·046 and the eugenol value (by absorption) to 79 per cent. The oil is faintly laevo-rotary, but never exceeds – 1° 30′; usually it is under – 1°. These characteristics, together with an estimation of the eugenol, are quite sufficient to control the purity of the oil.

Several methods have been suggested for the determination of the eugenol, none of which give absolutely accurate results, but from them useful comparative results may be obtained. Umney suggested the absorption of the eugenol in a Hirschsohn flask, as used for the examination of cassia oil, with a 10 per cent. solution of caustic potash. This strength was found to be too high, and a 5 per cent. solution is now preferred. The unabsorbed portion has a specific gravity of about 0·910, so that this should be allowed for, since the eugenol has a much higher specific gravity. Spurge prefers to saponify the esters first, and to make an allowance for them, but if a 5 per cent. solution be used, this method without any such allowance gives a close approximation to the total amount of eugenol, both free and combined being reckoned as eugenol. The globules of uncombined hydrocarbons have a great tendency to stick round the top of the flask and require some "coaxing" to rise and agglomerate in the neck of the flask. Heat will accelerate and assist this however. But the source of error lies in the fact that the aqueous solution of potash and potassium eugenate dissolves some of the sesquiterpene, which is thus reckoned as eugenol, and a too high result is obtained. The process proposed by Thom, although more tedious, gives more exact results. This depends on the conversion of the eugenol into benzoyl eugenol. The following are the details, which should be carefully observed in order to secure accurate results:—

About 5 grammes of clove oil are weighed into a beaker of

about 150 c.c. capacity, 20 grammes of 15 per cent. sodium hydroxide solution added, and then 6 grammes benzoyl chloride. On stirring, the solid mass of eugenol sodium salt at first formed goes into solution again as it is converted into benzoic ester, with evolution of much heat. In the course of a few minutes the reaction ends, and on cooling a solid crystalline mass of benzoyl eugenol is obtained. To this, 50 c.c. water is added, and the whole warmed on a water bath until the ester is completely melted to an oil, well stirred, cooled, and the clear supernatant aqueous solution filtered off. The crystalline mass is again washed with two successive quantities of 50 c.c. water, and the resulting impure benzoyl eugenol is recrystallised from alcohol, due allowance being made for its solubility in that medium. 25 c.c. of hot alcohol (90 per cent. by weight strength) are poured through the filter employed in the previous washing operations, in order to dissolve any adherent crystals, into the beaker, and the whole warmed upon the water bath until complete solution is effected. The solution is then cooled to 17° C., and the crystalline precipitate thrown upon a small weighed filter paper, filtered into a 25 c.c. cylinder, and washed with 90 per cent. alcohol until the filtrate exactly measures 25 c.c. The filter and crystals are then removed to a weighing bottle, dried at 100° C. until constant, and then weighed. From the total weight the weights of the filter paper and of the weighing bottle are deducted, from which the benzoyl eugenol is calculated. To the latter weight 0·55 grammes are added, being the weight of pure benzoyl eugenol dissolved by 25 c.c. 90 per cent. alcohol at 17° C. as determined by experiment.

This final quantity gives the amount of benzoyl eugenol, from which the amount of eugenol is easily calculated, eugenol having the formula $C_{10}H_{12}O_2$, and benzoyl eugenol $C_{17}H_{16}O_3$, so that $\frac{164x}{268y} \times 100$ = the percentage of eugenol,

if x equals the weight of benzoyl eugenol obtained, and y the weight of oil used in the estimation. Under these circumstances the eugenol content should not fall below 75 per cent., or if estimated by absorption with potash not below 82 per cent., usually from 85 to 90 per cent.

Thom has recognised the inaccuracy of the foregoing, and now recommends the following process. It consists in heating 5 grammes of the oil in a water bath with 20 c.c. of a 15 per cent. soda solution for 30 minutes. After allowing the hydrocarbons to separate, the eugenol soda solution is run off, and the hydrocarbons washed with dilute soda solution twice, the washings being added to the original soda solution. The reaction is now effected at water bath temperature with 6 grammes of benzoyl chloride. The whole is allowed to cool, and the crystalline mass transferred to a beaker with 55 c.c. of water. It is heated in order to melt the crystals, and well agitated with the water to wash the benzoyl eugenol. This washing is repeated twice. The crystalline mass is then transferred to a beaker with 25 c.c. of 90 per cent. alcohol, and warmed till complete solution takes place. The solution is allowed to stand till the bulk of the crystals have separated out, and is cooled to 17° and filtered through a paper 9 cm. in diameter, previously dried and tared. The filtrate measures about 20 c.c. and the crystals are washed with more alcohol until it measures 25 c.c. The paper and crystals are then dried in a weighing glass and weighed, the temperature of drying being not more than 101° C. The solubility allowance for 25 c.c. of alcohol is 0·55 gramme. The total eugenol is calculated from the formula

$$P = 4100 \frac{a + 0{\cdot}55}{67\ b}$$

where P is the percentage, a the weight of benzoyl eugenol obtained, and b is the weight of clove oil used.

Verley & Bolsing propose the following method. It

depends on the fact that acetic and other anhydrides react with phenols in excess of pyridine. Eugenol reacts readily forming eugenyl acetate and acetic acid, the latter combining with pyridine to form pyridine acetate. This compound reacts towards indicators such as phenol-phthalein in the same way as acetic acid and therefore a titration is possible. Verley & Bolsing use from 1 to 2 grammes of the oil, which is placed in a 200 c.c. flask, and 25 c.c. of a mixture of acetic anhydride (15 parts) and pyridine (100 parts). The mixture is heated for 30 minutes on a water bath, the liquid cooled, and 25 c.c. of water added. The mixture is well shaken and titrated with normal potash, using phenolphthalein as indicator. A blank experiment is carried out without the eugenol, and the difference between the titration figures in c.c. of normal alkali, multiplied by 0·582, gives the amount of eugenol in the sample taken.

As the boiling points of eugenol and caryophyllene are both high, no appreciable portion of the oil should distil below 245°, or even a few degrees higher. These tests will ensure the presence of a due proportion of eugenol, a point very necessary to take into account, because of the frequent abstraction of part of the eugenol, which is used in the manufacture of vanillin, or sold as pure eugenol. Absence of turpentine of petroleum is further ensured by the ready solubility of the oil in 90 per cent. alcohol. The oil from clove stems does not appreciably differ in its chemical composition from the above although its aroma is less delicate and it contains rather less eugenol. The oil is used to a certain extent in pharmacy, but to a much larger extent in the preparation of liqueurs and in perfumery, and has a very large commercial importance.

Schimmel & Co. give the following analyses of samples of clove oil:—

No.	Name and Origin.	Spec. Grav. 15°.	Opt. Rotation.	Index of Refraction 20°.	Phenol Content (determined with a 5 % sol. of NaOH).	Solubility.	Remarks.
1	Ol. caryoph. ang.	1·066	−0° 36′	1·53477	93·75 %	Soluble in 2·5 to 3 vol. and more 60 % alcohol	
2	Ol. caryoph. ang.	1·052	−0° 40′	1·53262	92 %	,, ,, 1 to 1·5 ,, ,, ,, 70 % ,,	
3	Ol. caryoph. arom. opt.	1·0525	−0° 36′	1·53287	90·5 %	,, ,, 1 to 1·5 ,, ,, ,, 70 % ,,	
4	Ol. caryoph. arom.	1·0287	−1° 12′	1·52766	74·5 %	,, ,, 0·5 ,, ,, ,, 70 % ,,	Inferior quality
5	Ol. caryoph. arom. opt.	1·0523	−0° 31′	1·53295	91·5 %	,, ,, 1 to 1·5 ,, ,, ,, 70 % ,,	
6	Ol. caryoph. arom.	1·0291	−1° 16′	1·52775	78 %	,, ,, 0·5 ,, ,, ,, 80 % ,,	,,
7	Oil of cloves B. P.	1·0501	−0° 40′	1·53146	88·2 %	,, ,, 1 to 1·5 ,, ,, ,, 70 % ,,	
8	Ol. caryoph. opt.	1·048	−0° 12′	1·53138	87·5 %	,, ,, 1 to 1·5 ,, ,, ,, 70 % ,,	
9	Ol. caryoph. 2 quality	1·0337	−1° 39′	1·52733	77 %	,, ,, 0·5 ,, ,, ,, 80 % ,,	,,
10	Oil of cloves, Zanzibar	1·0444	−0° 48′	1·53020	84·5 %	Soluble in 1 to 1·5 vol. 70 % alcohol; with more than 5 vol. cloudiness, which is only very slight with 10 vol. Soluble in 0·5 vol. and more 80 % alcohol.	,,
11	Oil of cloves, stems	1·0202	−1° 36′	1·52381	80 %	Soluble in 0·5 vol. 80 % alcohol; with more than 2 vol. cloudiness, which has again disappeared with about 9 vol.	,,

An oil distilled from clove leaves in the Seychelles had the following properties: specific gravity 1·049, optical rotation – 1° 40′, refractive index 1·5333, eugenol 87 per cent.

Oil of Bay.—This oil is the product of distillation of the leaves of *Pimenta acris* (*Eugenia acris*) and probably other closely allied species, plants flourishing in the West Indies. It is frequently described as being derived from *Myrcia acris*, but there is a doubt whether this is identical with *Pimenta acris*. The most prized oil comes from St. Thomas. The yield of oil obtained is from 2 to 3 per cent., and according to Markoe (*Pharm. Jour.* [3], viii., p. 1005) the oil comes over in two portions, firstly, a light oil which distils over rapidly, then a heavy oil distilling over more slowly. This of course means nothing more than that there are constituents of bay oil which have widely different boiling points. The fact that the *United States Pharmacopœia* of 1880 gave the specific gravity of bay oil as about 1·040, caused the heavier fractions to appear in commerce under that name. Pure normal distillates, however, have a specific gravity of ·965 to ·995, and oils with a higher specific gravity must be regarded as suspicious, being possibly adulterated with oil of cloves or oil of pimento. Occasionally distillates with a specific gravity of 1·020 or thereabouts are found with phenol values of 65 to 75 per cent., but these are rare.

The oil is slightly laevo-rotary, but should not exceed – 2°. Freshly distilled oil is soluble in 1 volume of 90 per cent. alcohol, but old oils are not so, on account of the alterations in the olefenic terpene, myrcene, which is present in the oil. The percentage of phenols (see *Oil of Cloves*) is an important factor in the valuation of the oil. In a genuine oil this figure should not fall below 60 per cent., when determined by absorption by 5 per cent. potash solution. The 1880 *United States Pharmacopœia* provided the following test to guard against adulteration with oils of cloves and pimento. "If to three

drops of the oil, contained in a small test tube, five drops of concentrated sulphuric acid be added, and, after the tube has been corked, the mixture be allowed to stand for half an hour, a resinous mass will be obtained. On adding to this mass 4 c.c. of diluted alcohol, vigorously shaking the mixture and gradually heating to the boiling point, the liquid should remain nearly colourless, and should not acquire a red or purplish-red colour."

Our knowledge of the chemistry of this oil is chiefly due to Mittmann (*Arch. Pharm.*, xxvii., p. 529), who first thoroughly investigated the oil, and to Power and Kleber, who cleared up several points left in an obscure state by the first-named chemist. According to Mittmann, pinene and probably dipentene are present, together with the principal constituent eugenol, and its methyl ether. He also believed a diterpene to be present, but this was probably formed by polymerisation during the distillations he effected. Power and Kleber do not agree that either pinene or dipentene are present, but state that the only terpene is *laevo*-phellandrene. The oxygenated compounds which these chemists state they have identified are eugenol, methyl-eugenol, chavicol, methyl-chavicol and citral. In addition to this they found a hydrocarbon of the formula $C_{10}H_{16}$ with the abnormally low specific gravity ·802. This, as well as other considerations, exclude the probability of this hydrocarbon being an ordinary terpene, and the chemists above named term it myrcene, and it is now recognised as an olefenic compound.

The oil is sometimes adulterated with oils of cloves and pimento, which cause an increase in the specific gravity, and should be tested for as given above. Turpentine is also added at times. This alters the optical rotation and specific gravity, and if the oil be distilled in a small fractionating flask the bulk of the turpentine is obtained in the early fractions. Assuming that pinene is not present at all in oil

of bay, turpentine may be detected by adding to, say, the first 10 per cent. distilled, an equal volume of amyl nitrite and two volumes of glacial acetic acid. The mixture is kept cold in ice and salt, and a mixture of equal parts of glacial acetic acid and hydrochloric acid is added drop by drop so long as a blue colour is developed. If pinene is present a white crystalline precipitate of pinene nitroso-chloride $C_{10}H_{16}NOCl$ is formed. 10 per cent. of turpentine can be detected with certainty in this way. The oil should, when freshly prepared, also be easily soluble in 90 per cent. alcohol, and when kept for some time should be soluble with a slight turbidity. This oil is largely employed in perfumery, especially in the preparation of the favourite toilet article, bay rum. It must not be confounded with the oil of Californian bay.

Eucalyptus Oil.—The oils distilled from the leaves of the various species of this enormous genus of the *Myrtaceæ* are in many cases so dissimilar that the generic term, eucalyptus oil, is meaningless unless the species is quoted. Several species, however, yield oils which are very similar to each other, and on this basis the *British Pharmacopœia* describes as eucalyptus oil the product obtained from *Eucalyptus globulus* and other species, giving definite characters of the oil, the two chief of which are the presence of a due proportion of cineol (eucalyptol) and the absence of appreciable quantities of the terpene phellandrene. The great variability in the oil from different trees will make it convenient to deal with this oil, firstly with reference to pharmacopœial oil, and afterwards with especial reference to the characters of the oils from those trees which in many cases are in no way similar to "*Eucalyptus oil, British Pharmacopœia*". It is now pretty well settled that whatever medicinal value this oil has—and it has been, and still is, used to a very large extent as a prophylactic against influenza—is due to the presence of cineol, or, as it was

originally known, eucalyptol. The *British Pharmacopœia*, 1885, had not entirely recognised this, and allowed oils to be used officially which might, and often did, contain very little eucalyptol. The 1898 *Pharmacopœia*, however, limits the specific gravity to ·910 to ·930, which ensures a high percentage of cineol, which has a specific gravity of ·930, the terpene phellandrene having a specific gravity of ·860, or thereabouts. The optical activity of the official oil is now limited to the extremes + 10° and − 10°, and as cineol is the optically inactive constituent of the oil, and the terpene is highly active, a due proportion of the former body is here again ensured. A positive test, however, is also given, although in such loose and vague language that it would bear considerable improvement. Scammell, of Adelaide, has patented a method for the preparation of pure cineol, dependent on the fact that this body forms a crystalline compound with phosphoric acid, which is decomposed by water, liberating the pure cineol. The *Pharmacopœia* requires that the oil shall become semi-solid when mixed with syrupy phosphoric acid. The presence of more than small quantities of phellandrene is guarded against by the well-known nitrite reaction, which is as follows: to 2 c.c. of the oil dissolved in 4 c.c. of glacial acetic acid, 3 c.c. of a saturated solution of sodium nitrite is added, with constant stirring, the oil being kept cold. The oil should remain liquid in the absence of phellandrene. Although none of these requirements in itself forms a direct quantitative control of the amount of cineol present, taken together they effectively prevent any oil which contains less than about 50 per cent. of cineol from being used officially. In the author's opinion the specific gravity limits are too stringent. He has examined a large number of eucalyptus oils with cineol contents of 45 to 52 per cent., which corresponded with the above requirements in every respect except that the

specific gravity was ·906 to ·910. The lower limit might well have been fixed at ·905.

The quantitative determination of the cineol present is a matter of importance. The earlier attempts in this direction gave distinctly too low results. The chief method adopted was a series of fractionations, retaining all those fractions distilling between 173° and 190°, cooling them to − 15°, filtering off the still liquid portion, retaining the crystals of cineol, refractionating the liquid portions and again freezing, subsequently weighing the crystallised cineol. An average loss of about 10 per cent., in the author's opinion, takes place in this process, assuming the oil to contain 50 to 60 per cent. of cineol. Scammell's process above-mentioned has been more successfully applied to the quantitative determination of cineol, and yields the most satisfactory results so far, although an error of several per cent. is scarcely avoidable.

There is some diversity of opinion on this matter, some chemists maintaining that a very close result is obtained, others that very large errors occur. In the author's opinion, in the hands of a careful worker, results accurate to within 3 per cent. can be obtained, so long as the cineol content is not below 40 per cent. If the amount of cineol is lower than this, the method is inapplicable, and the oil must previously be fractionated.

To a known weight of oil from 1 to 1½ times its weight of phosphoric acid of specific gravity 1·75 should be added, drop by drop, the oil being kept cold and continually stirred. The crystalline magma formed is pressed between filter paper, after as much as possible has drained off; and when the adherent terpenes and phosphoric acid have been removed as far as possible, the crystals are decomposed by hot water in a graduated tube. On cooling, the cineol is measured, and from its specific gravity (·930) the weight is easily calculated. The separated cineol should readily crys-

tallise on cooling to – 3°, otherwise it must be regarded as impure and the process repeated. Oils rich in cineol yield a correspondingly high fraction distilling between 170° and 190°.

The *American Pharmacopœia* directs that the oil is to be first diluted with petroleum ether, before treatment with phosphoric acid.

Schimmel & Co. recommend the absorption of the cineol by a 40-50 per cent. solution of resorcin in water, and reading the unabsorbed portion in the neck of a Hirschsohn flask. Although this method gives approximately accurate results in some cases, there is no doubt that the other constituents of the oil are, at times, the cause of a serious error in the absorption, and the really accurate determination of cineol is as yet an unsolved problem.

The great uncertainty regarding the term "eucalyptus oil" would be done away with by making the active ingredient, cineol or "eucalyptol" official in place of the oil. Its characters are well defined, and the article is easily made, and is a regular commercial product.

The chemistry and botany of this genus of the natural order *Myrtaceæ* require far more space than is available in the present work, to be dealt with thoroughly, consequently brief notes on the different species can only be given here. For fuller information the reader is referred to the late Baron von Müller's classic monograph *Eucalyptographia* and to the numerous monographs of Baker and Smith published in the *Proceedings* of the Royal Society of New South Wales during the past ten years. The majority of the species are natives of Australia and Tasmania. A few occur in New Zealand and in certain of the islands of the Indian Archipelago, and a fair quantity of oil, especially from *Eucalyptus globulus*, is now obtained from Algiers, California and the South of France and Spain. The chief species whose oils have been examined are the following:—

Eucalyptus amygdalina.—This is the "narrow-leaved peppermint" or "brown" or "white" peppermint of Victoria, and is also found in South Australia, Tasmania, Victoria, and New South Wales. It is not found in Western Australia however. It is an abundant, indeed one of the most abundant yielders of oil, as much as 4 per cent. being sometimes obtained from the leaves. It is one of the most colossal trees known, often reaching a height of 300 and sometimes 450 feet. At one time the oil was much esteemed, but as it contains very little cineol it has fallen into disfavour, and now commands a very low price. The oil, which is not particularly pleasant in odour, has a specific gravity of ·855 to ·890 and an optical rotation of – 25° to – 80°. The main constituent of the oil is the terpene phellandrene, besides which the only known constituent is cineol, which occurs to the extent of from 5 per cent. in the low to about 25 per cent. in the high gravity specimens. According to Baker and Smith, this account really refers to the oil from *E. amygdalina var. latifolia;* whilst the tree *E. amygdalina* yields an oil containing 45 per cent. of cineol.

Eucalyptus Backhousia (*Backhousia citriodora*) is one of the sweet-scented plants generally known as a eucalypt, but which probably belongs to a different genus altogether. The leaves yield up to 4 per cent. of oil of aromatic odour, not at all resembling what is usually termed eucalyptus oil, of specific gravity ·895 to ·902. The constituent to which it owes its lemon-melissa-like odour is citral. Its other constituents are undetermined, but it probably contains a little phellandrene.

Eucalyptus Baileyana.—This is one of the numerous trees known locally as "stringy bark," and is confined chiefly to the north of New South Wales and the adjacent southern portion of Queensland. The leaves yield about 1 per cent. of oil, of a melissa-like odour, which, however, is partially

covered by the cineol present. Its specific gravity is from ·890 to ·920 (specific gravities of ·940 to ·980 have been given, but these are hardly possible). It appears to contain up to 25 or 30 per cent. of cineol, some citral, and phellandrene.

Eucalyptus capitellata.—This tree is found in Victoria and Queensland. Its oil, which has not been examined, has an odour recalling that of peppermint. It has a specific gravity ·915, and contains about 35 to 40 per cent. of cineol and traces of a crystalline body, which has been named eudesmol.

Eucalyptus camphora.—This is the Swamp gum of New South Wales. The oil has a specific gravity 0·916, and contains pinene, cineol and eudesmol.

Eucalyptus cneorifolia.—This eucalypt, one of the Mallees, is chiefly found in Kangaroo Island, South Australia. It is a comparatively small plant, seldom reaching more than 12 to 15 feet in height. It is known locally as the "narrow-leaved eucalyptus". The plant was originally looked upon as a variety of *Eucalyptus oleosa*, but it is now understood to be a separate species. The oil came into commerce some few years ago under the name of *oleosa*, but is quite different from the oil which was originally known under the same name. The oil is very rich in cineol, and has the high specific gravity ·915 to ·925, or even higher. Its optical activity is small, seldom exceeding 4° or 5° either way. It has a secondary odour recalling that of cumin. It contains from 50 to 70 per cent. of cineol and a small quantity of cumic aldehyde. This oil is much valued as a medicinal oil, and conforms admirably to pharmacopœial requirements.

Eucalyptus corymbosa.—This is the New South Wales "bloodwood". It is found in this colony and in Queensland, chiefly near the sea coast. Its leaves yield about 4 per cent. of oil of specific gravity about ·880. It has an aro-

matic odour, according to Maiden, recalling that of lemon and roses. Sawyer states that it is rich in cineol, but this is incorrect. It contains a small quantity of cineol, and probably aldehydes of the geraniol series.

Eucalyptus crebra.—This is one of the many so-called "iron barks" of Queensland. Its oil is bright yellow, and very rich in eucalyptol, closely resembling that from *Eucalyptus globulus.*

Eucalyptus Dawsoni.—This tree yields an oil of specific gravity 0·9414, and contains no cineol, but phellandrene and a sesquiterpene.

Eucalyptus dealbata.—This plant is confined to the drier portions of Queensland and New South Wales. Its oil, which is yielded to the extent of nearly 3 per cent. by the leaves, has a pleasant mellisa odour, and belongs to the class of sweet-scented eucalyptus oils. By many it is considered to possess a finer odour than any of the other eucalypts. The oil has a specific gravity of ·885 to ·900, and contains citronellal and either citronellol or geraniol. If the leaves be dried before distillation the oil is of a different character, and is said to have a specific gravity of over ·940.

Eucalyptus dextro-pinea.—This species has been described quite recently by Baker. It is a "stringy bark" of New South Wales, known as "messmate". Its botanical characters do not differ greatly from several other already described species, but its oil, which is yielded to the extent of about ·8 per cent., is characterised by containing a large amount of dextro-pinene. The oil is dextro-rotary, and of specific gravity ·873 to ·876. Small quantities of aldehydes were also detected (see *Eucalyptus laevo-pinea*).

Eucalyptus dumosa.—This plant is one of the Mallees (dwarf eucalypts forming the "scrub" of parts of Victoria, New South Wales and South Australia). The oil is of a good quality from a medicinal point of view, having a specific

gravity of about ·900 to ·912, and containing from 30 to 50 per cent. of cineol. Its odour is strongly camphoraceous.

Eucalyptus eugenoïdes.—The leaves of this tree yield about ·7 per cent. of oil of agreeable odour. Its specific gravity is about ·905 to ·910, and its rotary power + 4° to + 6°. It contains from 25 to 35 per cent. of cineol and not any, or at most very little, phellandrene.

Eucalyptus globulus.—This tree, from which a typical eucalyptus oil is obtained, is the Tasmanian "blue gum". (Blue gum however is a name applied to a number of other eucalypts in New South Wales, Victoria and Western Australia.) This plant was discovered by Labillardière in Tasmania in 1792, and introduced into Europe in 1856 by Ramel. It is a native of Tasmania and Victoria, although found to a certain extent in other colonies. The fresh leaves yield from ·8 to 1·5 per cent. of oil of a light yellow colour, exceedingly rich in cineol. Eucalyptol, as it was then called, and as it is often termed to-day, was discovered by Cloez in this oil. The fact that this oil was regarded in Europe as the typical eucalypt yielding a medicinal oil, together with the occurrence of such numerous and closely similar species in Australia, account for the fact that eucalyptus leaves from various trees were indiscriminately mixed and distilled, the resulting product being marked oil of *Eucalyptus globulus.* Hence the difference observed by various chemists in the properties of this oil. The pure globulus oil, which is now a reliable commercial article, has a specific gravity of ·910 to ·930, and contains from 50 per cent. to 65 per cent. of cineol. It is dextro-rotary, from + 1° to + 10° (rarely up to + 15°). In addition to cineol it contains dextro-pinene, camphene, traces of ethyl and amyl alcohols and valeric, butyric and caproic aldehydes. This oil is the most valued of all the medicinal eucalyptus oils of commerce. Schimmel & Co. have isolated a crystalline compound melting at 88·5°, boiling at

283° and of specific rotary power – 35° 29′. It is a sesquiterpene alcohol of the formula $C_{15}H_{26}O$. They have also isolated an alcohol, $C_{10}H_{16}O$, which is possibly pinocarveol.

Eucalyptus goniocalyx.—This tree is known in Victoria as the "spotted gum" or "white gum," but in New South Wales it is usually spoken of as "blue gum". The oil is bright yellow, of suffocating odour, of specific gravity ·915 to ·920, and contains some cineol.

Eucalyptus gracilis.—This tree inhabits the same districts as *Eucalyptus dumosa*, and is also found in Queensland. Its oil contains a fair proportion of cineol, and its cultivation has attracted some attention in Victoria.

Eucalyptus hæmostoma.—This is one of the many white gums of New South Wales and Queensland. The leaves yield about 2 per cent. of a nearly colourless oil, which is said by Dr. Bancroft to possess an odour intermediate between peppermint and geranium. Its specific gravity is ·880 to ·890. Cymene and cumic aldehyde have been detected in the oil, and possibly menthone also occurs. Schimmel & Co. consider it resembles cumin oil in odour.

Eucalyptus incrassata.—This plant is cultivated to a certain extent in Victoria, as yielding an oil with a fairly high cineol content. It has not, however, been closely examined.

Eucalyptus laevo-pinea.—This plant has recently been described as a new species by Baker. It is the silver top stringy bark of New South Wales. Very slight differences of a botanical nature exist between this tree and *Eucalyptus dextro-pinea* (*q.v.*), but the oil differs in that it consists chiefly of *laevo*-pinene, and contains only a very small quantity of cineol. The specific gravity of the oil is about ·873. Smith, who has examined these oils (*Eucalyptus dextro-pinea* and *laevo-pinea*), most unjustifiably suggests calling the pinenes he has separated from them by the names eucalyptene and

eudesmene respectively. As a matter of fact the hydrocarbons he separated were merely ordinary pinene with some little impurity, so that the rotary powers were not exactly coincident with those known for this hydrocarbon, but to duplicate names in this free and easy fashion must only tend to restore that confusion which existed in the terpene group before Wallach took up the task of correctly classifying them.

Eucalyptus leucoxylon is a "white gum" of Victoria and South Australia. It is also known as "boxwood" or "mountain ash". It is also found in Queensland and New South Wales. Its leaves yield rather over 1 per cent. of oil of specific gravity ·920 to ·925 with a fairly high cineol content.

Eucalyptus longicornis.—This plant is the morell tree of Western Australia, which is found on the sources of the Swan river, and onwards towards the east. Its leaves yield a high percentage of oil, but this has not yet been thoroughly examined.

Eucalyptus longifolia.—This tree, known as the "woolly-but," is found in New South Wales and in Gippsland, Victoria. The oil has a camphoraceous odour, but the sample of which an examination has been recorded had the high specific gravity ·940, and was possibly adulterated.

Eucalyptus loxophleba.—This tree is the York gum of Western Australia, so named on account of its frequent occurrence in the neighbourhood of York. It is found all over the eastern slopes of the Darling Range, and forms one of the valued timber trees of the colony. The oil has been examined by the author, who found it to contain only about 15 per cent. of cineol. It is dextro-rotary, about +5° and has a specific gravity ·883. It contains phellandrene and another terpene, together with a considerable amount of aldehydes or ketones. It possesses a very irritating and offensive odour.

Eucalyptus Macarthuri.—The oil from this plant has the following characters: Specific gravity about ·920 to ·930; optical rotation + 1°. It contains eudesmol and geranyl acetate.

Eucalyptus macrorhyncha.—According to Baker and Smith, the leaves of this plant yield about ·3 per cent. of oil of a reddish-brown colour and of agreeable odour. Its specific gravity is ·927. The oil contains up to 53 per cent. of cineol, with traces of phellandrene and esters. The crystalline compound melting at 74° discovered by the above-named scientists, and termed by them eudesmol, is also present in considerable quantity.

Eucalyptus maculata var. citriodora.—This tree, the "citron-scented" eucalyptus, is found along the coast of Queensland and as far south as Port Jackson. It is a variety of the New South Wales "spotted gum," *Eucalyptus maculata* (which itself possesses very little odour). This variety yields the typical scented eucalyptus oil. The yield from the leaves is from 1 to 4 per cent. of an oil of melissa-like odour, of specific gravity ·870 to ·905, and slightly dextro-rotary to + 2°. It contains a very large quantity of citronellal, one specimen, according to Schimmel & Co., having been found to contain as much as 95 per cent. It also contains geraniol. This oil is of a most pleasant odour, and is admirably suited for soap perfumery, possessing a far more delicate odour than ordinary citronella oil, which it somewhat resembles in its general characteristics.

Eucalyptus microcorys.—This is the sallow wood of New South Wales or "turpentine tree" of Queensland. It yields from 1 to 2 per cent. of an oil of specific gravity ·895 to ·930. Cineol appears to be the only well-ascertained constituent, but according to some, the oil, when properly prepared, forms an excellent perfume.

Eucalyptus obliqua.—This tree is generally known as

"strong bark" or "stringy bark" in Tasmania and Victoria. It is also found in New South Wales and South Australia. The leaves yield a fair quantity of oil of specific gravity ·895 to ·915 and optical rotation about − 7°. It contains both cineol and phellandrene in varying proportions.

Eucalyptus odorata.—Two trees are known by this name, the "white box" and the "peppermint" of the southern colonies of Australia. The leaves of the latter yield about 1·5 per cent. of an oil of specific gravity ·900 to ·925. It contains cineol, phellandrene and cumic aldehyde, and probably another aldehyde. It is said to be used to a certain extent in soap perfumery in Australia. The "white box" yields a very small amount of oil of specific gravity ·900 to ·922 containing much cineol.

Eucalyptus oleosa.—This tree forms one of the Mallee scrub group, which are all fairly rich in cineol. It is well known in Victoria and South Australia and is also found in the interior extra-tropical parts of Western Australia. The leaves yield about 1·3 per cent. of an oil, of specific gravity ·905 to ·930 and optical activity − 5° to + 5°. It is very rich in cineol. According to Baron Müller, it is the best known solvent for fossil resins, and "is unique for many technological applications". This oil is not identical with much of the so-called *Oleosa* oil of commerce, which is in reality obtained from *Eucalyptus cneorifolia.*

Eucalyptus piperita.—This is the New South Wales peppermint tree. Its leaves yield a large quantity of oil, but this is not well known in commerce, although it is manufactured in at least one district in New South Wales. It contains a ketone which resembles menthone, which has been named piperitone.

Eucalyptus populifolia.—This is the "bimbil box" of New South Wales, Queensland, and the northern territories of South Australia. The oil is bright red and contains

cineol and cumic aldehyde. In odour it resembles cajuput oil.

Eucalyptus punctata.—Baker and Smith have described this as a variety of *Eucalyptus tereticornis*, known in New South Wales as grey gum. The yield of oil obtained was from ·63 to 1·19 per cent., its specific gravity ·9122 to ·9205. Of nine oils examined, two were *laevo*-rotary, from − 0° 55′ to − 2° 31′, and seven were *dextro*-rotary, from + 0° 32′ to + 4° 29′. The cineol content varied from 46·4 to 64·5 per cent., and no phellandrene was detected.

Eucalyptus Planchoniana.—This species is of limited occurrence, being found only in the northern parts of New South Wales and in South Queensland. The yield of oil, which has a specific gravity ·915, is very low. It has been suggested as a soap perfume, its odour somewhat resembling citronella.

Eucalyptus resinifera.—This tree is known as the swamp gum. The oil yielded by the leaves is of a brilliant yellow colour, of specific gravity about ·900 and optical rotation − 15° to − 20°. It contains a fair quantity of cineol.

Eucalyptus rostrata.—This is a "red gum" common to all the colonies of the Australian mainland, being known as the "flooded gum of the interior". It is one of the most widely distributed eucalypts on the continent, and its timber has supplied more material for telegraphs, railways, bridges, etc., than perhaps any other tree in Australia. This tree, too, is the best known of all trees to the Australian explorers, for on it nearly all the old landmarks, camp locations and "signs" of the early explorers may be found cut. The tree has been introduced into Cochin China and Algeria, in both of which places it flourishes well. The oil has a somewhat powerful odour of valeric aldehyde, which body, together with much cineol, exists in the oil. This has a specific gravity ·915 to ·930 and an optical rotation of − 2° to + 13°.

Eucalyptus rudis.—This tree, according to Maiden, is known as a "blue gum" of Western Australia. The author has traversed the whole of the regions in which this tree is found, however, and finds that it is usually known as the "flooded gum". *Eucalyptus rostrata* just referred to is known as the "flooded gum of the interior," or commonly merely "flooded gum," and occurs on the littoral just south of the Murchison, whilst *Eucalyptus rudis* (as well as *Eucalyptus decipiens*), which occurs in the south-western portion of the colony, may be referred to as the "flooded gum of the south-west". The leaves yield a large quantity of oil, but its properties require examination.

Eucalyptus Risdonia.—The oil from the leaves of this tree has a pleasant odour. Its specific gravity is ·910 to ·925, and its optical rotation – 2° to – 6°. Phellandrene and cineol, the latter in good proportion, have been found in the oil.

Eucalyptus salubris.—This is one of the Western Australian timber trees, its wood being largely used on the goldfields, where it is known as the gimlet gum. Its leaves yield, according to Müller, 4 per cent. of oil. Its specific gravity is 0·902, and optical rotation – 6°. It contains pinene, cymene, cineol, geranyl acetate and aromadendral.

Eucalyptus Staigeriana. — This is the well-known "lemon-scented iron bark" of Queensland. The leaves when bruised have a strong verbena odour; indeed the oil closely resembles the latter in general properties. It is stated in the *Pharm. Journal* ([3], x., 212) that it can be distinguished from verbena oil by its lower specific gravity. This, however, is not so. The extraordinary statement also occurs that it has a specific gravity ·871, or, when freed from moisture, ·880, which means that by removing water with a higher specific gravity, the residual oil also increases in gravity! The characteristic odour is due to

citral, which appears to be the chief constituent of the oil.

Baker and Smith have recently examined this oil and found it to have a specific gravity 0·871, refractive index 1·4871, and to contain laevo-limonene, geraniol, geranyl acetate and citral.

Eucalyptus Stuartiana.—This tree, which is found in Queensland, yields a yellow oil, with a strong odour of cymene. Very little, if any, cineol is present.

Eucalyptus terticornis.—This is one of the Queensland "red gums". It yields an oil somewhat resembling oil of zedoary in odour, and contains little or no cineol. It is of little value.

Eucalyptus tesselaris.—This tree yields an oil of a dark brown colour, and with an odour recalling benzoic acid. It contains no cineol.

Eucalyptus uncinata.—This tree is found in Western and South Australia, Victoria and South Australia. It is one of the Mallees. The yield of oil is not very high, but the resulting oil contains a fair amount of cineol.

From the above brief remarks on the eucalyptus oils which are much known, it will be seen that they, broadly speaking, fall into three chief groups. The sweet-scented or perfume oils are few in number, and are typically represented by *Eucalyptus maculata var. citriodora* and *Eucalyptus Staigeriana.* The medicinal oils—those which contain a high percentage of cineol (eucalyptol)—are the most important group however; the requirements of the 1898 *British Pharmacopœia* narrow these down to comparatively few, which must have the characters therein described, and are therefore *British Pharmacopœia* oils. The typical oil—speaking from a popular point of view—of this class is that of *Eucalyptus globulus,* but it is a mistaken idea to think that there are not other oils of just as great value. Indeed,

the oil of *Eucalyptus globulus* has its reputation from its label, as probably the majority of importations in the earlier days of this oil were mixtures, often without any globulus oil, in spite of their labels. The facts should be noted that not only are several other oils in accordance with the *British Pharmacopœia* requirements, but that many oils which do not quite agree with the limits prescribed by that standard are valuable oils of high cineol content. The third class embraces those oils which contain little or no cineol, and which are of very small value as compared with the other oils. The type of these oils is, perhaps, that of *Eucalyptus amygdalina*. The recognised value of cineol, and the ease with which it can be prepared, result in the manufacture of pure cineol, which is known commercially as eucalyptol. In the author's opinion, eucalyptus oil as an *official* drug might well be replaced by eucalyptol, whose properties are very definite, *viz.*, specific gravity ·930; optically inactive; solidifying at low temperatures and re-melting at − 1°; boiling at 176°. There is only one danger in this, *viz.*, that if eucalyptol were made official the oil would naturally be removed from the *Pharmacopœia*. The public, however, know the oil so well that they would continue to demand it, and any of the almost valueless oils, such as *Eucalyptus amygdalina*, could then be sold with impunity.

Smith has described several hitherto unknown bodies which he finds present in various eucalyptus oils. Amongst these are the following. Piperitone: this compound is a ketone of the formula $C_{10}H_{18}O$, which he finds in oils from *E. piperita* and *E. dives* and *E. radiata*. It resembles menthone, and further evidence is necessary to establish its individuality. Aromadendrene: this body is a sesquiterpene boiling at 260° to 265° and of specific gravity 0·925. It has so far not yielded any crystalline derivatives, and is provisionally named aromadendrene. Aromadendral is an aldehyde

resembling cumic aldehyde in odour. It is an oil of specific gravity 0·953 at 22°, optical rotation – 86°, boiling at 219°. Its formula is $C_9H_{12}O$. It yields crystalline derivatives and may therefore be regarded as a fresh chemical individual. Eudesmol or eucalyptus camphor is best prepared from *E. macrorhyncha*. It is a crystalline compound melting at 79° to 80°, and of the formula $C_{10}H_{16}O$. Eudesmic acid is an acid obtained from the esters of some eucalyptus oils. It has the formula $C_{14}H_{18}O_2$.

Smith has classified a number of eucalyptus oils from the point of view of their refractive indices. The following table covers his figures.

The refractive indices of the following constituents occurring in the ordinary types of eucalyptus oils are:—

Eucalyptol (Schimmel)	1·45961
Pinene (Wallach)	1·46553
Phellandrene (Wallach)	1·488
Cymene (Brühl)	1·48465
Aromadendral	1·5141 at 16° C.
Piperitone	1·4893 at 16° C.
Sesquiterpene (prepared by distillation)	1·5116 at 16° C.

These constituents vary much in amount in the oils of the several species, but it is possible to form groups such as the eucalyptol group, the phellandrene group, etc. The refractive index of the predominant constituent will, of course, influence the result, but there is a marked uniformity between the members of the several groups, agreeing strongly with the indications suggested by the study of the leaf venations.

Eucalyptol-pinene oils; phellandrene usually absent. Refractive index mostly above 1·47 and below 1·48.

No.	Species.	Refractive index n_d 16° C.	Specific gravity $\frac{16°}{16°}$ C.	Specific refractive energy $\frac{n_d - 1}{d}$.	Solubility in alcohol (·8722 at 15·5° C.) 1 volume requires	10 times solubility × refractive index.
1	*E. Smithii*	1·4706	·9238	·5094	1·05	15·44
	Ditto, oil of "suckers"	1·4707	·9151	·5144	1·15	16·91
	Ditto, com. crude 5·08	1·4669	·9172	·5112	1·05	15·42
2	*E. Bridgesiana*	1·4723	·9327	·5064	1·05	15·46
3	„ *Risdoni*	1·4733	·9373	·5049	1·05	15·47
4	„ *pulverulenta*	1·4686	·9280	·5049	1·1	16·15
5	„ *dealbata*	1·4705	·9268	·5077	1·1	16·17
6	„ *stricta*	1·4711	·9254	·5090	1·1	16·18
7	„ *polyanthema*	1·4736	·9346	·5067	1·1	16·21
8	„ *oleosa*[1]	1·4746	·9319	·5093	1·1	16·22
9	„ *cordata*	1·4695	·9265	·5067	1·15	16·89
10	„ *cinerea*	1·4706	·9198	·5116	1·15	16·91
11	„ *populifolia*	1·4709	·9246	·5093	1·15	16·91
12	„ *Cambagei*[1]	1·4720	·9243	·5106	1·15	16·92
13	„ *sideroxylon*	1·4725	·9219	·5125	1·15	16·93
14	„ *pendula*	1·4732	·9337	·5068	1·15	16·94
15	„ *bicolor*	1·4734	·9266	·5109	1·15	16·94
16	„ *Maideni*	1·4736	·9253	·5117	1·15	16·94
17	„ *cneorifolia*[1]	1·4747	·9194	·5163	1·15	16·96
	Ditto, F. & Co., crude	1·4774	·9375	·5092	1·1	16·25
18	*E. maculosa*	1·4741	·9278	·5109	1·17	17·24
19	„ *Morrisi*	1·4693	·9191	·5106	1·2	17·68
20	„ *squamosa*[1]	1·4692	·9202	·5099	1·2	17·68
21	„ *globulus*	1·4720	·9243	·5106	1·2	17·66
	Do. Platypus bd. 4 yrs.	1·4697	·9153	·5131	1·15	16·90
	Do. do. 8 years old	1·4738	·9392	·5044	1·15	16·95
22	*E. polybractea*[1]	1·4736	·9197	·5149	1·2	17·68
	Do. commer. dist. 6·04	1·4686	·9286	·5046	1·0	14·68
	Do. do. crude dist. 7·05	1·4692	·9282	·5055	1·05	15·42
	Do., same oil rectified	1·4676	·9254	·5053	1·05	15·41
23	*E. hemilampra*	1·4735	·9310	·5086	1·2	17·68
24	„ *longifolia*	1·4738	·9249	·5122	1·2	17·68
25	„ *intertexta*	1·4748	·9328	·5092	1·2	17·69
26	„ *Behriana*	1·4765	·9272	·5139	1·2	17·72
27	„ *Stuartiana*	1·4709	·9194	·5122	1·25	18·88
28	„ *eugenioides*	1·4747	·9220	·5148	1·25	18·43
29	„ *amygdalina*	1·4760	·9104	·5228	1·25	18·45
30	„ *punctata*[1]	1·4774	·9297	·5135	1·25	18·46
31	„ *Rossii*	1·4741	·9202	·5152	1·35	19·90
32	„ *resinifera*	1·4755	·9194	·5172	1·35	19·91
33	„ *Seeana*	1·4706	·9146	·5145	1·37	20·14
34	„ *camphora*	1·4733	·9072	·5217	1·4	20·62
35	„ *rostrata* var. *borealis*	1·4747	·9251	·5131	1·4	20·64
36	„ *viminalis* var. (*a*)	1·4711	·9169	·5138	1·45	21·33
37	„ *goniocalyx*	1·4746	·9097	·5218	1·8	26·54
38	„ *ovalifolia* v. *lanceolata*	1·4711	·9119	·5166	2·0	29·42
39	„ *salmonophloia*[1]	1·4738	·9069	·5225	3·5	51·58
40	„ *quadrangulata*	1·4692	·9075	·5170	4·0	58·76
41	„ *Bosistoana*	1·4732	·9175	·5158	5·0	73·66
42	„ *melliodora*	1·4706	·9041	·5205	6·0	88·23
43	„ *redunca*	1·4720	·9092	·5191	6·0	88·32
44	„ *conica*	1·4733	·9259	·5112	6·0	88·39
45	„ *propinqua*[1]	1·4788	·9035	·5299	8·0	118·30
46	„ *odorata*[1] (Faulding)	1·4775	·9150	·5218	insoluble 10 volumes 70% alcohol	soluble 1 volume 80% alcohol
47	„ *occidentalis*[1]	1·4774	·9128	·5230		
48	„ *dumosa*[1]	1·4760	·9130	·5213		
49	„ *microcorys*	1·4747	·9059	·5240		
50	„ *gracilis*[1]	1·4771	·9107	·5239		
51	„ *paludosa*	1·4773	·9095	·5248		

Pinene oils; phellandrene absent. Refractive index above 1·47 and below 1·48.

No.	Species.	Refractive index n_d 16° C.	Specific gravity $\frac{15}{15}$° C.	Specific refractive energy $\frac{n_d - 1}{d.}$	
52	*E. botryoides*	1·4787	·8802	·5439	None soluble in less than 7 volumes of 80 per cent. alcohol
53	„ *calophylla*	1·4788	·8751	·5471	
54	„ *dextropinea*	1·4741	·8806	·5383	
55	„ *diversicolor*	1·4747	·9134	·5197	
56	„ *lævopinea*	1·4769	·8964	·5320	
57	„ *saligna*	1·4760	·8940	·5324	
58	„ *Wilkinsoniana*	1·4774	·9016	·5295	

Pinene-sesquiterpene oils; phellandrene absent. Refractive index above 1·48.

No.	Species.	Refractive index n_d 16° C.	Specific gravity $\frac{15}{15}$° C.	Specific refractive energy $\frac{n_d - 1}{d.}$	
59	*E. affinis*[1]	1·4921	·9270	·5301	None soluble in less than 1 volume 80 per cent. alcohol, the majority insoluble in 10 volumes 80 per cent. alcohol
60	„ *apiculata*	1·4934	·9123	·5408	
61	„ *Baeuerleni*	1·4841	·8890	·5445	
62	„ *corymbosa*[1]	1·4895	·8867	·5520	
63	„ *eximia*	1·4889	·8999	·5433	
64	„ *intermedia*[1]	1·4878	·8838	·5519	
65	„ *lactea*	1·4898	·8794	·5570	
66	„ *maculata*	1·4861	·9085	·5380	
67	„ *nova-anglica*	1·4900	·9062	·5407	
68	„ *paniculata*	1·4801	·9096	·5278	
69	„ *patentinervis*	1·4948	·8784	·5633	
70	„ *rubida*	1·5011	·9089	·5513	
71	„ *tesselaris*	1·4881	·8962	·5446	
72	„ *trachyphloia*[1]	1·4901	·8915	·5497	

Oils in which aromadendral is a pronounced constituent; phellandrene is absent. Refractive index above 1·48.

73	*E. albens*	1·4836	·9188	·5263	With the exception of No. 74, all are soluble in either 1 or 2 volumes of 80 per cent. alcohol
74	„ *hemiphloia*	1·4910	·9084	·5405	
75	„ *marginata*	1·4946	·9112	·5428	
76	„ *punctata* var. *didyma*	1·4868	·9068	·5368	
77	„ *rostrata*	1·4896	·9018	·5429	
78	„ *salubris*	1·4841	·9013	·5358	
79	„ *tereticornis*	1·4934	·9308	·5301	
80	„ *viridis*	1·4828	·9027	·5348	
81	„ *Woollsiana*	1·4895	·8998	·5440	

Phellandrene oils containing piperitone. Refractive index above 1·48, several above 1·49.

No.	Species.	Refractive index n_d16° C.	Specific gravity $\frac{15}{15}$° C.	Specific refractive energy $\frac{n^d-1}{d}$.	
82	*E. coriacea*	1·4902	·9120	·5375	Mostly insoluble in 10 volumes 80 per cent. alcohol; none more soluble than with 1 volume 80 per cent. alcohol
83	„ *delegatensis*	1·4881	·8645	·5646	
84	„ *dives*	1·4894	·8883	·5509	
85	„ *fraxinoides*	1·4908	·8762	·5601	
86	„ *Luehmanniana*	1·4937	·8846	·5581	
87	„ *obliqua*[1]	1·4934	·8944	·5528	
88	„ *oreades*	1·4945	·8935	·5534	
89	„ *piperita*	1·4838	·9221	·5247	
90	„ *radiata*	1·4863	·8814	·5517	
91	„ *Sieberiana*	1·4896	·8947	·5461	
92	„ *vitrea*	1·4882	·8967	·5384	

Phellandrene oils in which the sesquiterpene is a pronounced constituent. Refractive index is above 1·48 and in some instances above 1·5.

93	*E. acmenoides*	1·5065	·9266	·5466	No. 102 is the only oil more soluble than with 1 volume 80 per cent. alcohol; a large number were insoluble in 10 volumes 80 per cent. alcohol
94	„ *angophoroides*	1·4881	·9207	·5301	
95	„ *capitellata*	1·4828	·9176	·5261	
96	„ *crebra*	1·4844	·8989	·5388	
97	„ *Dawsoni*	1·5144	·9528	·5399	
98	„ *fastigata*	1·4873	·8948	·5446	
99	„ *Fletcheri*[1]	1·4881	·8882	·5495	
100	„ *gomphocephala*	1·4815	·8752	·5501	
101	„ *hæmastoma*	1·5013	·9196	·5451	
102	„ *macrorrhyncha*	1·4802	·9166	·5239	
103	„ *melanophloia*	1·4950	·8959	·5526	
104	„ *microtheca*	1·4895	·8866	·5521	
105	„ *nigra*	1·4871	·8838	·5511	
106	„ *ovalifolia*	1·4921	·8911	·5522	
107	„ *Planchoniana*	1·4878	·9166	·5322	
108	„ *pilularis*	1·4961	·8924	·5559	
109	„ *robusta*	1·4801	·8899	·5395	
110	„ *siderophloia*	1·5000	·9081	·5506	
111	„ *sideroxylon* v. *pallens*	1·4884	·9167	·5328	
112	„ *stellulata*	1·4902	·8766	·5589	
113	„ *viminalis*	1·4855	·9088	·5342	
114	„ *virgata*	1·5015	·9352	·5363	

Oils not classified; containing geraniol and its acetic acid ester, citral, citronellal, etc.

115	*E. citriodora*	1·4651	·8887	·5233	Soluble in 1·5 vols. 70% alco. at 16° C.
	Do. Mr. Ingham, Qld.	1·4678	·8829	·5298	
116	*E. Macarthuri*	1·4793	·9271	·5172	Soluble in 1·3 volumes 70% alcohol
	Do. cont. 64·73% ester	1·4763	·9252	·5148	
	Do. cont. 68·8% ester	1·4768	·9287	·5134	
117	*E. Staigeriana*	1·4871	·8708	·5594	Insoluble in 6 volumes 80% alcohol
118	„ *aggregata*	1·5062	·9701	·5128	Insoluble in 10 vols. 80% alcohol

[1] Denotes the presence of a small amount of aromadendral in the oil.

The following valuable classification of this family of oils is reproduced from details published by Messrs. Schimmel & Co. as the results of examination of a collection of the oils supplied by Baker and Smith.

No.	Botanical name.	Vernacular name.	Origin.	Average yield of oil in %.	Principal chemical constituents.
1.	*E. tessellaris* F. v. M.	Moreton Bay, Ash	Narrabri, N.S.W.	0·151	Pinene, sesquiterpene
2.	*E. trachyphloia* F. v. M.	Bloodwood	Murrumbo, N.S.W.	0·199	Pinene, sesquiterpene
6.[1]	*E. eximia* R. T. B.	White Blood-wood	Springwood, N.S.W.	0·462	Pinene
7.	*E. botryoides* Sm.	Bastard Ma-hogany	Milton, N.S.W.	0·086	d-Pinene
8.	*E. robusta* Sm.	Swamp Ma-hogany	La Perouse, N.S.W.	0·161	Pinene
9.	*E. saligna* Sm.	Blue Gum	Gosford, N.S.W.	0·241	Pinene
10.	*E. nova-anglica* D. & M.	Black Pepper-mint	Walcha, N.S.W.	0·51	Terpenes
11.	*E. umbra* R. T. B.	A Stringybark	Lismore, N.S.W.	0·1615	Pinene, also an acetic acid ester
12.	*E. dextropinea* R. T. B.	Stringybark	Barber's Creek, N.S.W.	0·798	d-Pinene
13.	*E. Wilkinsoniana* R. T. B.	Small-leaved Stringybark	Barber's Creek, N.S.W.	1·01	l-Pinene
14.	*E. lævopinea* R. T. B.	Silver-top Stringybark	Rylstone, N.S.W.	0·66	l-Pinene
15.	*E. Bäuerleni* F. v. M.	Brown Gum	Monga, N.S.W.	0·328	Terpenes, eucalyptol, chiefly the former
16.	*E. propinqua* D. & M.	Grey Gum	Woodburn, N.S.W.	0·235	
17.	*E. affinis* D. & M.	Black Box	Grenfell, N.S.W.	0·259	
18.	*E. paludosa* R. T. B.	Swamp Gum	Barber's Creek, N.S.W.	0·197	
19.	*E. lactea* R. T. B.	Spotted Gum	Ilford, N.S.W.	0·557	Terpenes
21.	*E. intertexta* R. T. B.	Gum or Red Gum	Nyngan, N.S.W.	0·395	Pinene, eucalyptol

[1] The missing numbers are also wanting in the original.

No.	Botanical name.	Vernacular name.	Origin.	Average yield of oil in %	Principal chemical constituents.
22.	*E. maculata* Hook.	Spotted Gum	Currawang Creek, N.S.W.	0·169	Pinene, eucalyptol, chiefly the former
25.	*E. quadrangulata* D. & M.	Grey Box	Milton, N.S.W.	0·684	Pinene, eucalyptol
26.	*E. conica* D. & M.	Box	Parkes, N.S.W.	0·587	Pinene, eucalyptol
27.	*E. Bosistoana* F. v. M.	Box	Barber's Creek, N.S.W.	0·968	Pinene, eucalyptol, chiefly the former
28.	*E. eugenioides* Sieb.	White Stringybark	Canterbury, N.S.W.	0·742	Terpenes, eucalyptol
30.	*E. resinifera* Sm.	Mahogany	Gosford, N.S.W.	0·302	Pinene, eucalyptol
31.	*E. polyanthema* Sieb.	Red Box	Pambula, N.S.W.	0·825	
32.	*E. Behriana* F. v. M.	Mallee Gum	Wyalong, N.S.W.	0·614	
33.	*E. Rossi* R. T. B. and H. G. S.	White or Brittle Gum	Bathurst, N.S.W.	0·65	Pinene, eucalyptol, also piperitone
34.	*E. pendula* A. Cunn.	Red Box	Nyngan, N.S.W.	0·67	Pinene, eucalyptol, chiefly the latter
35.	*E. dealbata* A. Cunn.	Cabbage or Montain Gum	Condobolin, N.S.W.	0·856	Pinene, eucalyptol, chiefly the latter
37.	*E. rostrata* Schl. var. *borealis* R. T. B. and H. G. S.	River Red Gum	Nyngan, N.S.W.	1·001	Pinene, eucalyptol
38.	*E. maculosa* R. T. B.	Spotted Gum	Bungendore, N.S.W.	0·846	Pinene, eucalyptol
39.	*E. camphora* R. T. B.	Sallow	Delegate, N.S.W.	0·886	Eucalyptol
40.	*E. punctata* D. C.	Grey Gum	Canterbury, N.S.W.	0·781	Pinene, eucalyptol
41.	*E. squamosa* D. & M.	Ironwood	National Park, N.S.W.	0·643	Eucalyptol
42.	*E. Bridgesiana* R. T. B.	Apple or Woollybutt	Ilford, N.S.W.	0·619	

No.	Botanical name.	Vernacular name.	Origin.	Average yield of oil in %.	Principal chemical constituents.
43.	*E. goniocalyx* F. v. M.	Montain Gum	Monga, N.S.W.	0·881	Eucalyptol
44.	*E. bicolor* A. Cunn.	Bastard Box	St. Mary's, N.S.W.	0·52	
45.	*E. viminalis* var. (*a*)		Crookwell, N.S.W.	0·701	Pinene, eucalyptol, benzaldehyde (?)
46.	*E. populifolia* F. v. M.	Poplar-leaved Box	Nyngan, N.S.W.	0·758	Eucalyptol
47.	*E. longifolia* Link.	Woollybutt	Canterbury, N.S.W.	0·535	
48.	*E. Maideni* F. v. M.	Blue Gum	Barber's Creek, N.S.W.	1·304	
49.	*E. globulus* Labill.	Blue Gum	Jenolan, N.S.W.	0·745	
50.	*E. pulverulenta* Sims.		Bathurst, N.S.W.	2·22	
51.	*E. cinerea* F. v. M.	Argyle Apple	Barber's Creek, N.S.W.	1·20	Eucalyptol, some valeric acid ester
51*a*.	*E. cordata* Labill.		Tasmania	2·32	Eucalyptol
54.	*E. Morrisii* R. T. B.	Grey Mallee	Gerilambone, N.S.W.	1·69	
55.	*E. Smithii* R. T. B.	Gully Ash or White Top	Monga, N.S.W.	1·434	
56.	*E. sideroxylon* A. Cunn.	Red Flowering Ironbark	Liverpool, N.S.W.	0·537	Pinene, eucalyptol
57.	*E. cambagei* D. & M.	Bastard Box or Bundy	Bathurst, N.S.W.	0·735	Eucalyptol, some aromadendral
58.	*E. polybractea* R. T. B.	Blue Mallee	Wyalong, N.S.W.	0·135	Pinene, eucalyptol, aromadendral
59.	*E. dumosa* A. Cunn.	White Mallee	Coolabah, N.S.W.	1·00	Terpenes, eucalyptol, aromadendral
60.	*E. oleosa* F. v. M.	Red or Water Mallee	Nyngan, N.S.W.	0·97	Pinene, eucalyptol, aromadendral

No.	Botanical name.	Vernacular name.	Origin.	Average yield of oil in %.	Principal chemical constituents.
61.	*E. cneorifolia* D. C.		Kangaroo Island		Pinene, eucalyptol, aromadendral
62.	*E. stricta* Sieb.	Mountain Mallee	Blue Mountains, N.S.W.	0·494	Eucalyptol
63.	*E. melliodora* A. Cunn.	Yellow Box	Rylstone, N.S.W.	0·676	Pinene, eucalyptol, frequently also phellandrene
64.	*E. ovalifolia*, var. *lanceolata* R. T. B.	Red Box	Camboon, N.S.W.	0·579	Pinene, eucalyptol, phellandrene
64*a*.	*E. Risdoni* Hook. f.	Risdon or Drooping Gum	Tasmania	1·848	Eucalyptol, phellandrene, piperitone
66.	*E. punctata* D.C., var. *didyma* R. T. B. & H. G. S.		Barber's Creek, N.S.W.	0·402	Pinene, eucalyptol, aromadendral
67.	*E. gracilis* F. v. M.	A Mallee	Gunbar, N.S.W.	0·901	Pinene, eucalyptol, aromadendral; the terpenes predominate
68.	*E. viridis* R. T. B.	Green Mallee	Gerilambone, N.S.W.	1·06	Terpenes, a small quantity aromadendral
69.	*E. Woollsiana* R. T. B.	Mallee Box	Gerilambone and Nyngan, N.S.W.	0·449	Aromadendral
70.	*E. albens* Mig.	White Box	Rylstone, N.S.W.	0·101	Aromadendral
71.	*E. hemiphloia* F. v. M.	Box	Belmore, N.S.W.	0·554	Pinene, eucalyptol, aromadendral
72.	*E. viminalis* Labill.	Manna Gum	Cadia, N.S.W.	0·354	Phellandrene, eucalyptol
73.	*E. rostrata* Sch.	Murray Red Gum	Albury, N.S.W.	0·299	Chiefly terpenes, also eucalyptol and aromadendral; sometimes phellandrene
74.	*E. ovalifolia* R. T. B.		Rylstone, N.S.W.	0·216	Pinene, eucalyptol, phellandrene
75.	*E. Dawsoni* R. T. B.	Slaty Gum	Bylong, N.S.W.	0·172	Phellandrene, sesquiterpene

No.	Botanical name.	Vernacular name.	Origin.	Average yield of oil in %.	Principal chemical constituents.
76.	*E. angophoroides* R. T. B.	Apple-topped Box	Towrang, N.S.W.	0·185	Terpenes, among which phellandrene
77.	*E. fastigata* D. & M.	Cut Tail	Monga, N.S.W.	0·263	Pinene, phellandrene, eudesmol
78.	*E. macrorhyncha* F. v. M.	Red Stringybark	Rylstone, N.S.W.	0·272	Terpenes, eucalyptol, eudesmol
79.	*E. capitellata* Sm.	Brown Stringybark	Canterbury, N.S.W.	0·103	Terpenes, small quantities of eucalyptol
80.	*E. nigra* R. T. B.	Black Stringybark	Woodburn, N.S.W.	0·0295	Phellandrene
81.	*E. pilularis* Sm.	Blackbutt	Belmore, N.S.W.	0·13	Terpenes, also an as yet unknown alcohol
83.	*E. acmenoides* Sch.	White Mahogany	Lismore, N.S.W.	0·358	Terpenes, among which phellandrene
84.	*E. fraxinoides* H. D. & J. H. M.	White Ash	Monga, N.S.W.	0·985	Terpenes, chiefly phellandrene
85.	*E. Fletcheri* R. T. B.	Lignum Vitæ or Box	Thirlmere, N.S.W.	0·352	
86.	*E. microtheca* F. v. M.	Coolybah or Tangoon	Narrabri, N.S.W.	0·150	
87.	*E. hæmastoma* Sm.	White or Scribbly Gum	Barber's Creek, N.S.W.	0·241	Phellandrene, sesquiterpene
89.	*E. crebra* F. v. M.	Narrow-leaved Ironbark	Rylstone, N.S.W.	0·159	Pinene, phellandrene, eucalyptol
92.	*E. piperita* Sm.	The Sydney Peppermint	Gosford, N.S.W.	0·627	Pinene, phellandrene, eucalyptol, eudesmol and piperitone
93.	*E. amygdalina* Labill.	Messmate	Moss Vale, N.S.W.	3·393	Phellandrene, eucalyptol and piperitone
94.	*E. vitrea* R. T. B.	White Top Messmate	Crookwell, N.S.W.	1·48	Phellandrene, eucalyptol
95.	*E. Luehmanniana* F. v. M.		National Park, N.S.W.	0·289	Phellandrene
96.	*E. coriacea* A. Cunn.	Cabbage Gum	Ilford, N.S.W.	0·452	Phellandrene, piperitone

No.	Botanical name.	Vernacular name.	Origin.	Average yield of oil in %.	Principal chemical constituents.
97.	*E. Sieberiana* F. v. M.	Mountain Ash	Barber's Creek, N.S.W.	0·421	
98.	*E. creades* R. T. B.	A Mountain Ash	Lawson, N.S.W.	1·16	
99.	*E. dives* Sch.	Broad-leaved Peppermint	Fagan's Creek, N.S.W.	2·233	Phellandrene, piperitone
100.	*E. radiata* Sieb.	White Top Peppermint	Monga, N.S.W.	1·641	
101.	*E. delegatensis* R. T. B.	White Ash, Silver Top Mountain Ash	Delegate Mountain, N.S.W.	1·76	
102.	*E. obliqua* L'Hér.	Stringybark	Monga, N.S.W.	0·677	Phellandrene, a small quantity aromadendral
103.	*E. stellulata* Sieb.	Lead Gum	Rylstone, N.S.W.	0·293	Phellandrene
104.	*E. Macarthuri* H. D. and J. H. M.	Paddy River Box	Wingello, N.S.W.	0·112	Geranyl acetate
106.	*E. virgata* Sieb.		Springwood, N.S.W.	0·283	Eudesmol
107.	*E. patentinervis* R. T. B.	Mahogany	Belmore, N.S.W.	0·254	Terpenes, citral and an as yet unknown alcohol
108.	*E. apiculata* R. T. B. and H. G. S.		Berrima, N.S.W.	0·296	Terpenes, piperitone
109.	*E. citriodora* Hook.	Citron-scented Gum	Sydney, N.S.W.	0·586	Citronellal

Cajuput Oil.—This oil is distilled from the leaves of several species of *Melaleuca*, myrtaceous shrubs growing abundantly in the Indian archipelago, the Malay peninsula, and other places. Most of the oil of commerce is yielded by *Melaleuca minor* or by *Melaleuca leucadendron*. The oils from these two trees can scarcely be distinguished. The *British Pharmacopœia* gives *Melaleuca leucadendron* (*Melaleuca cajuputi*). A great portion of the oil is distilled on the islands of Bouru and Banda, whence it is brought to Macassar and the neighbourhood for shipment. The bulk of the oil is exported in wine bottles, although shipment in drums, to save the excessive freight, has been resorted to. The oil has a powerful camphoraceous odour, due largely to its high cineol content. It is usually of a green colour, generally due to contamination with copper, but can be obtained white by re-distillation. The specific gravity usually varies from ·920 to ·930, although the *Austrian*, *Italian* and *Japanese Pharmacopœias* allow a rather lower limit. The present edition of the *British Pharmacopœia* gives ·922 to ·930. It is now well recognised that 0·917 is a permissible limit for genuine oils from the districts above mentioned. The oil is almost optically inactive, usually varying from 0° to − 2°. The refractive index is about 1·4650 to 1·4680. Normal oil contains up to 65 per cent. of cineol. In addition to this body, to which the oil owes its value, terpineol and terpinyl acetate have been found, and, according to Voiry (*Jour. Pharm. Chim.*, 1888, p. 149), butyric, valeric and benzoic aldehydes and probably laevopinene. The low specific gravity of many commercial samples is accounted for by adulteration with turpentine, or by abstraction of the cineol. The oil is not used to any extent internally, but is employed externally as a stimulant and anti-spasmodic. Eucalyptus oil with a high cineol content is well able to replace it for most purposes. Genuine

cajuput oil should contain at least 50 per cent. of cineol, as estimated by the phosphoric acid process.

The oil from *Melaleuca viridifolia*, a plant growing abundantly in New Caledonia, has been examined by Bertrand. The leaves when fresh yield about 2·5 per cent. of a pale yellow oil, generally known as "essence de Niaouli," with an odour resembling that of cajuput. The sample examined (*Comptes Rendus*, cxvi., p. 1070) had a specific gravity ·922 and a rotary power + 0° 42′. Traces of valeric and benzoic aldehydes are present in this oil, the greater part of which consists of cineol and a terpene, probably pinene. A little terpineol is also probably present, and possibly traces of limonene. Maiden, and later Baker and Smith, have described a number of species of *Melaleuca* indigenous to Australia. The physical properties of the oils from them are as follows:—

	Specific Gravity.	*Boiling Point.*	*Rotation.*
Melaleuca decussata .	·938	183°-209°	—
Melaleuca ericifolia .	·899-·902	149°-184°	+ 26°
Melaleuca linarifolia .	·903-·913	175°-258°	+ 2°-+ 11°
Melaleuca Wilsonii . .	·925	—	—
Melaleuca uncinata .	·925	175°-180°	+ 1° 40′
Melaleuca leucadendron var. lancifolia . .	·955	—	- 3° 38′
Melaleuca acuminata .	·892	—	- 15° 20′
Melaleuca thymifolia .	·9134	172°-214°	+ 2° 6′

Myrtle Oil.—This oil is distilled from the leaves of *Myrtus communis*, probably a native of the south of Europe, although possibly it was introduced here from Western Asia. So long ago as 1867 Gladstone examined this oil, but his results are of little value to-day. The specific gravity of the oil varies from ·895 to ·915, or ·920 at times. The rotation is to the right, from + 10° to + 30°. Jahns has shown that this oil contains dextro-pinene, cineol and a camphor of the formula $C_{10}H_{16}O$. Probably dipentene also is present. Under the name "myrtol," the fraction of the oil

boiling between 160° and 170° has been introduced into commerce. It is not a definite compound, and probably possesses little value. Von Soden and Elze have found in the higher boiling fractions of this oil an alcohol, $C_{10}H_{18}O$, which they term myrtenol. It occurs chiefly as its acetic ester. It is a colourless oil of strong myrtle odour, of specific gravity 0·985, optical rotation + 49° 25′, and boiling at 220°. The oil is sometimes used medicinally, but probably a little cineol would be more useful than myrtle-leaf oil in any case where it might be required.

Cheken-leaf Oil is the product of distillation of the leaves of *Myrtus cheken*, indigenous to Chili. The yield is about 1 per cent. of a pale yellowish-green oil, much resembling ordinary myrtle oil. According to Weiss, its specific gravity is about ·880, and its optical rotation about + 20°; it consists of pinene (75 per cent.), cineol (15 per cent.), and substances not further examined.

N. O. Rosaceæ.

Oil of Roses.—Of the numerous varieties of the rose, only a very few are used for the preparation of oil or "otto" (attar) of roses. Climate and soil have so marked an influence on this plant, that a few varieties are found to grow to perfection in special localities, and these alone are cultivated for the purpose of obtaining the oil. Not only does the sweet and characteristic odour of rose vary much amongst the different varieties, but many of these are practically odourless, and some even objectionable in this respect.

The "rose garden of the world," as it has been fittingly called, is situated in the Balkans, and from the slopes of the Balkans nearly the whole of the otto of rose of commerce is obtained. The most important centre of the industry is Kezanlik. The area under cultivation is included between the 24th and 26th degrees of longitude east, and the 42nd

and 43rd degrees of latitude north. The geological formation is chiefly syenite, the decomposition of which has produced a very fertile soil. The roses flourish best in sandy sun-exposed slopes, with a south or south-eastern aspect. The most important districts are (1) the department of Stara-Zagora, including the cantons of Kezanlik, Nova-Zagora and Stara-Zagora; (2) the department of Pazardjik, chiefly the canton of Pechtera; (3) the department of Philippopolis, including the cantons of Karlovo, Tchirpan, Novo-Selo and Brezovo. The flowers are gathered before they commence

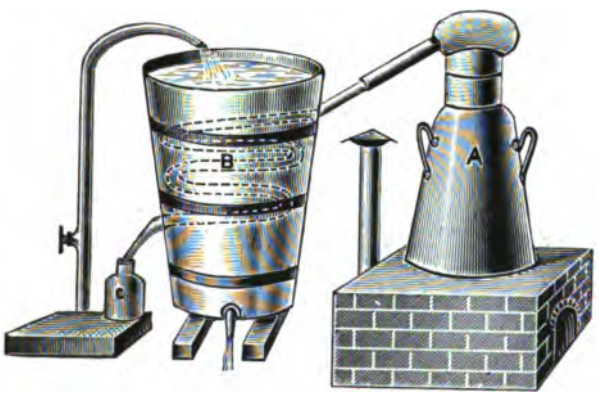


FIG. 21.—A, copper alembic; B, condenser; C, receiver.

to open, in the early morning just before sunrise, and the picking continues till ten or eleven o'clock, or on cloudy days during the whole day, as it is important that the roses should not be picked when the sun's heat is on them. A garden of an acre when well planted will yield about 100 pounds of flowers every day for three weeks. The roses are carried to the distilleries, which are very numerous, and distilled as quickly as possible. However, if the flowers come in too quickly they are sometimes left for twenty-four hours before being distilled, the resulting oil being thereby

impaired in value. The distilleries are primitive buildings, sometimes little better than wooden sheds. On one side the stills are kept in rows. These are copper alembics about 3 to 5 feet in height, resting on a furnace built of bricks. The average content of each still is about 20 gallons, the charge usually being 10 kilos of flowers and 75 litres of water.

The condenser is a straight or worm tube passing through a vat of water, into which cold water continually runs. A brisk fire is kept up for an hour to an hour and a half, and when 10 litres of liquid are obtained the fire is drawn. At times 15 litres are distilled over, but the result is an otto containing a larger amount of stearoptene. The still is then opened and the spent petals, or rather flowers, for the green plants are seldom separated, are thrown away, and the residual hot water is returned to the still with cold water to make up the 75 litres, with a fresh charge of flowers. This operation is repeated until, as a rule, 40 litres of rose water have been collected. These 40 litres are now distilled, and the first 5 litres are collected in a long-necked flask. The residual 35 litres are used for distilling fresh flowers. The 5 litres distilling over are cloudy, and the oil drops gradually rise and collect in the neck of the flask. When it has all risen, it is removed by a small tin funnel with a tiny orifice for the water to be drawn off. The yield is variable, a warm humid spring with intervals of strong sunshine being more favourable than an uninterrupted hot dry season. The average yield in Bulgaria is about 1 kilo of otto from 3,000 kilos of rose leaves. The rose cultivated in this district is *Rosa damascena*, a red rose, but the hedges of the plantations are often made up of *Rosa alba*. The latter are often distilled with the red roses, but as the resulting oil contains more stearoptene than that of the *Rosa damascena*, it is rarely distilled alone. The difficulties in acquiring exact knowledge on many points connected with

oil of roses has been largely enhanced by the fact that adulteration is very largely practised. The usual adulterant used to be the so-called Indian geranium oil, and in spite of stringent regulations, and seizure of smuggled geranium oil, the practice still goes on to an enormous extent. Purified geraniol has, however, now taken the place of the crude geranium oil. It is surprising that an industry of so much importance should have been allowed to go on for so many years fettered by two such great evils; firstly, the enormous adulteration practised, secondly, the defective methods of preparation, resulting in the spoiling of the fine odour of much of the otto. Although climate and soil have so great an influence on the yield and quality of the oil, there can be no doubt that there are localities where rose cultivation and distillation could be carried on in a scientific as well as an honest way.

Formerly the Turkish dealers were responsible for the greater part of the adulteration, but now the small growers come in for their share of the illicit profits, and not only do they add the adulterant to the distillate, but frequently sprinkle the leaves with geraniol before distillation, believing that they so obtain a better "blend".

The value of a pure oil depends on the quality of the flowers used and on the care taken in distillation. It also depends on the amount of solid stearoptene present, for this portion of the oil is quite inodorous.

The value of otto in the locality of its distillation is gauged almost entirely by its melting point. Consequently spermaceti or even paraffin wax has been added to counteract the reducing influence of the liquid geranium oil. Recently, too, guaiacum wood oil (so-called), an oil of fine odour which solidifies with a fine crystalline structure at ordinary temperatures, and consists of bodies much resembling those in oil of roses, has been used as an adulterant.

In this connection it may be mentioned that no standard for the quantity of stearoptene present in natural rose oil can be fixed, as climatic conditions appear to influence the ratio of the solid to the liquid portion very greatly. From 10 to 20 per cent. occurs in Bulgarian oil, whereas that obtained in the south of France, in England and in Germany, has been stated to contain from 25 to 65 per cent. of stearoptene. In the case of so high a content as the latter figure it is certain that the oil was not prepared in the normal way, probably being the result of the distillation of rose water. The example set by one or two of the best distillers, however, is now taking effect, and pure otto of rose can be obtained by dealing with a house of repute. Further, steam distilleries are being erected, and so far as one can judge at the present moment, an otto of different properties is obtained when distilled by steam instead of in the usual manner (*vide infra*).

Roses are cultivated to a very large extent in the south of France in the neighbourhood of Grasse, Cannes and Nice. Here, however, the variety most cultivated is *Rosa centifolia*. The flowers are used chiefly for the preparation of rose water and rose pomade, very little oil being manufactured, and practically the whole of this is used in France itself, seldom appearing to any great extent on the English market. Here the flowers are also picked in the early morning, as many as 150 tons of flowers being gathered on a single day in the province of the Alpes Maritimes. The petals are usually entirely separated from the green parts in France. The otto produced here is of very exquisite odour.

In Germany, Messrs. Schimmel & Co. have laid out extensive plantations near Klein-Miltitz, and although the natural resources of climate and soil are not so favourable here as in Bulgaria or Southern France, the scientific and careful way in which the oil is obtained, to a certain extent counterbalances

this, and a fairly fine otto is obtained. In Algeria, a small amount of otto is produced, but the yield is less than in Bulgaria. In Persia and Cashmere, however, it is said that nearly one pound of otto is obtained from 1,500 to 2,000 pounds of petals.

Oil of roses is not an easy oil to form an opinion upon with any degree of certainty. Gross adulterations can easily be detected, but judicious admixtures are less easy to deal with. The *British Pharmacopœia* requires that the specific gravity at 30° should be between ·856 and ·860, and the congealing point from 19·4° to 22·2°. These figures are not correct. Normally distilled otto has a specific gravity 0·850 to 0·858, rarely rising to 0·860 at $\frac{30°}{15°}$. The refractive index is a valuable figure to determine and should fall between 1·4580 and 1·4650. Geraniol raises this figure perceptibly. Simmons gives 187 to 194 as the iodine absorption value for pure Bulgarian otto of rose. The oil is nearly inactive optically, and + 1° to − 4° may be regarded as safe limits. Alcohol is sometimes added as an adulterant, but can be diluted in the watery extract, when the resultant oil will be found to have altered in its physical characters, such as refractive index and gravity. To exemplify the difference in the physical properties of certain oils produced in other districts, the following may be quoted. A Persian oil, believed by Schimmel & Co. to be pure, gave the following figures:—

Specific gravity at 25°	= ·8326
Optical rotation . .	= − 9° 7′
Congealing point .	21·5°

Dupont has given the optical rotation for French oil up to − 8°, and this is amply confirmed by other observers.

Jeancard and Satie (*Bull. Soc. Chim. de Paris*, 1904, 934) have published a paper dealing with the analysis of otto of rose. They have distilled a sample from the flowers of *Rosa centifolia* freed from the petals, with the following results:—

Congealing point	8°
Stearoptene	51·13 per cent.
Specific gravity at 15°	0·8704
Rotatory power	– 41°
Melting point of stearoptene	14°
Free acid value	6·12
Saponification No.	22·4
Alcohols	13·99 per cent.
Citronellol	13·56 per cent.

An otto obtained from the complete flowers grown at Cannes had the following character. The oil melted at 25·5° and contained 33 per cent. of stearoptene. The stearoptene was removed and the oil then had the following characters :—

Specific gravity at 15°	0·879
Rotatory power	– 3°
Solubility in 70 per cent. alcohol	1 in 2
Alcohols	88·55 per cent.
Citronellol	22·4 per cent.

An otto from the tea rose is said to contain 72 to 94 per cent. of stearoptene, although the melting point was only 23·5°. The stearoptene contained two bodies, one melting at 14° and the other at 40°. The authors recommend valuing otto of roses by its stearoptene and citronellol contents. They operate as follows :—

Ten grammes of the otto are weighed into a beaker and 50 c.c. of acetone are added. The liquid is cooled to – 10° or thereabouts, without shaking, and then filtered through a funnel kept in a refrigerating mixture. The stearoptene is washed several times with cold acetone, and dried on the weighed filter paper *in vacuo* over sulphuric acid. They proceed to give the following as the limits for twelve samples of Bulgarian otto of rose :—

Melting point	19°-21°
Stearoptene	18-23 per cent.
Specific gravity of stearoptene-free oil at 15°	0·886-0·888
Rotatory power	– 1° – 3°
Solubility in 70 per cent. alcohol	1 in 1·5
Acid value	1·2

Saponification value	10-12
Alcohols	88-84 per cent.
Citronellol	80-40 „

They consider that all pure French ottos should have between 30 and 35 per cent. of stearoptene, and 20 to 23 per cent. of citronellol in the eleoptene, whilst Bulgarian otto should have from 18 to 23 per cent. of stearoptene, and 30 to 40 per cent. of citronellol in the eleoptene. The author is not prepared to agree with these figures in their entirety. Firstly, the relation between the melting points and the stearoptene values does not appear to be at all probable, and secondly, the limits given must have been taken from far too few samples to be representative. For instance, 19° to 21° is too narrow for the melting point of the otto, and the specific gravity of the eleoptene will vary outside the narrow limits of 0·886 to 0·888. The characters of the stearoptene should always be examined.

Burgess finds that for the estimation of the stearoptene 85 per cent. alcohol gives the most accurate results. He finds that 5 grammes of the otto (in these experiments he also used 5 grammes of a standard solution of stearoptene in geranium oil, and in citronellol—see table), in 25 c.c. of the solvent—or if a weaker alcohol be used 50 c.c.—is the most suitable quantity for the determination. Solution is effected by means of heat, and the liquid is then cooled in ice for 5 or 6 hours. The stearoptene is then filtered off on paper over a filter pump and washed, once if 85 per cent. alcohol be used, twice if a weaker spirit be employed; the paper with the separated stearoptene is then dried *in vacuo* over sulphuric acid for 12 hours. It is not necessary to tare the filter paper, since the stearoptene can be removed in one cake from the paper, and weighed on a watch glass.

The appended table (p. 404) shows the results obtained with the various solvents on otto of rose, and on standard

Stearoptene Determinations. Burgess's Table.

Solvent.	Otto of Rose.		Geranium Oil.						Citronellol.					
			5 °/₀		10 °/₀		15 °/₀		5 °/₀		10 °/₀		15 °/₀	
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
75 °/₀ Alcohol .	[1]16·4	[1]14·2 °/₀	[1]5·26	[1]5·28 °/₀	[1]10·64	[1]10·54 °/₀	[1]16·22	[1]15·64 °/₀	[1]4·50	[1]4·46 °/₀	[1]9·84	[1]9·78 °/₀	[1]13·94	[1]14·26°/₀
85 °/₀ „ .	—	—	4·52	4·42	9·56	9·76	15·26	15·14	4·34	4·30	9·10	9·10	13·18	13·78
90 °/₀ „ .	15·04	14·74	4·26	4·16	—		13·72	13·76	3·68	3·74	8·92	8·96	13·00	13·72
94 °/₀ „ .	14·4	14·1	3·84	3·88	8·58	8·56	13·40	13·44	3·20	3·16	8·24	8·50	13·00	12·66
					4·82	4·66					4·62	4·62		
Acetone . .	13·8	14·0	3·68	3·84	1·88	2·62	13·38	13·44	3·12	3·08	2·14	2·00	12·16	12·16
					6·70	7·28					6·76	6·62		
		8·46												
Acetic Ether .		4·63		—		—		—		—		—		—
		13·09												

[1] In all these cases the precipitate and filter paper were distinctly oily, showing imperfect solution of the eleoptene.

solutions of stearoptene in geraniol, and in citronellol. With acetone, he found in some cases, a further separation of stearoptene took place, so that he has recorded the results in the form of the two weighings of the stearoptene where necessary.

The addition of geranium oil (Indian) or geraniol may cause a rise in the specific gravity sufficient to bring that of the oil outside the limits given above, but in moderate quantity may avoid detection in this way. The optical rotation will scarcely be affected, but the congealing point will be lowered, and if the original otto contained only a moderate quantity of stearoptene, this figure will be reduced below the minimum allowable for pure oils. An examination of the stearoptene thus, as mentioned above, becomes necessary. By addition of alcohol and freezing as there described, the stearoptene can be almost entirely separated on a filter pump and washed with alcohol and finally dried. It should then melt between 32° and 37°, usually at 33° to 34°. Spermaceti, and most samples of paraffin wax, will cause this to be rather higher, as will also "guaiacum wood" oil if present in more than very small quantities. Salol and antipyrin have been found as solid adulterants.

Spermaceti or stearin will be easily detected, whilst paraffin wax or the solid constituent of guaiacum wood oil (which is of an alcoholic nature) are not so easy of detection. As the stearoptene of pure rose oil consists of hydrocarbons, no fatty acids will be obtained by saponification, whereas spermaceti and stearin will yield on saponification and decomposition of the resulting salts with hydrochloric acid, palmitic and stearic acids respectively, which may be identified by their melting points (palmitic acid from 55° to 62°, and stearic acid from 62° to 68°). Paraffin will be indicated by the more granular structure of its crystals than that of the normal stearoptene, whilst the solid portion of guaiacum wood oil consists chiefly

of a solid alcohol and will yield an acetyl figure, which is not the case with the normal stearoptene.

The following tables are given by Schimmel:—

	1. German Oil, Miltitz, 1900.	2. German Oil, Miltitz, 1900.	3. Bulgarian Oil (Kazanlik).	4. Bulgarian Oil (Kazanlik).	5. Oil from Philippople from our expert. Distilled by himself.	6. Purchased.
Specific gravity at 40°	0·8372	0·8304	0·8566	—	—	—
Specific gravity at 30°	0·8438	0·8360	0·8598	0·8594	0·8634	0·8614
Rotatory power at 30°	−0° 44′	−0° 52′	−2° 20′	−2° 43′	−2° 58′	−2° 36′
Congealing point	+29·0°	+30·0°	+20·0°	+20·4°	+19·6°	+20·4°
Stearoptene - content	28·50%	39·97%	18·62 %	18·83 %	18·49 %	20·55 %
Acid number	2·3	0	0	2·3	0	0
Sap. number	4·5	10·4	11·03	7·0	11·1	10·1
Sap. number after acetylisation	188·7	171·14	216·0	204·1	214·7	211·0
Sap. number after formylation	59·21	47·9	92·9	96·8	104·0	100·6
Calculated from these figures:— Total alcohols $C_{10}H_{18}O$	60·44 %	54·00 %	70·38 %	66·27 %	70·37 %	68·98 %
Citronellol in the formylation product	16·49 %	13·34 %	25·88 %	26·96 %	28·97 %	28·03 %

Values obtained direct in analysing oils free from stearoptene:—

Spec. gravity at 15°	0·8857	0·8886	—	0·8862	0·8774	—
Rotatory power 20°	−0° 56′	−1° 2′	—	−2° 49′	−2° 38′	—
Sap. number after acetylisation	271·55	261·64	—	255·8	254·8	—
Sap. number after formylation	74·70	81·22	—	125·28	127·4	—
Total alcohol	93·78 %	90·80 %	—	87·04 %	86·63 %	—
Citronellol	20·81 %	22·63 %	—	34·90 %	35·50 %	—

The percentage of free alcohols in the oil usually varies from 70 to 75 per cent., estimated as geraniol, by acetylation. Geranium oil gives from 75 to 95 per cent., so that no definite

information is yielded in this way. Dietze (*Sudd. Apotheker Zeitung*, xxxvii. [89], p. 835) strongly recommends the acid and ester values to be determined by titration, and saponification with semi-normal alcoholic potash. This gives the following figures (in percentages of potash) :—

	Acid.	*Ester.*	*Saponification.*
German rose oil . .	·21	·65	·86
Bulgarian . . .	·12	·80	·92
,, . . .	·14	·75	·89
French geranium .	·68	4·79	5·47
,, ,, . .	·50	5·41	5·91
African ,, . .	·75	4·56	5·31
Spanish ,, . .	·98	7·19	8·17
Indian ,, . .	·15	3·10	3·25

Whilst there is no doubt that the ester value of most geranium oils is higher than that of rose oil, the above figures are not comprehensive enough, and the indications obtained would be of very little value in the case of admixtures of considerable quantities of geranium oil.

Of the chemistry of oil of roses, although fairly well understood now, much controversial matter has been written. Eckart ("Inaugural Dissertation," Breslau, 1891) states that a small quantity of ethyl alcohol exists in the oil. If this is so, which Poleck denies, it is in all probability the result of fermentation taking place in the leaves, by keeping them too long before distillation. Markovnikoff and Reformatsky originally stated that the liquid portion of rose oil consisted chiefly of an alcohol of the formula $C_{10}H_{20}O$, which they termed roseol. Poleck and Eckart claimed that this alcohol had the formula $C_{10}H_{18}O$, and was identical with geraniol. They however proposed the name rhodinol (which was applied to an alcohol $C_{10}H_{20}O$ from geranium oil by Barbier and Bouveault) for it. Bertram and Gildemeister then showed that the alcohols from rose oil were in reality a mixture of two bodies, of which they agreed that geraniol $C_{10}H_{18}O$ was

the chief constituent. Tiemann and Schmidt explained these differences, proving that the alcohols consisted of about 75 per cent. of geraniol $C_{10}H_{18}O$ and 25 per cent. of an alcohol $C_{10}H_{20}O$, which was identical with that obtained by reducing citronellic aldehyde. Hence they naturally insisted on the name citronellol. Much confusion has unnecessarily been caused by various chemists giving names to alcohols they had isolated from different oils in an impure state, and refusing to alter these names after it had been conclusively proved that they were, when pure, identical with already known bodies. Lemonol, rhodinol, réuniol and roseol are all either geraniol or citronellol, or mixtures of them. Traces of esters of these two alcohols, and of free acids resulting from their decomposition also occur. The stearoptene was regarded by Markovnikoff as consisting of a single paraffin hydrocarbon of the formula $C_{16}H_{34}$, melting at 37°, but Schimmel & Co. have separated two hydrocarbons melting at 22° and 41° respectively, from the stearoptene. This has been confirmed by Dupont and Guerlain. These chemists suggest that the ester, which appears to be found in larger quantity in French oils than in any other, is an important odoriferous constituent, and is destroyed by repeated distillation with water. They separated the liquid portion of the oil and found it had an optical rotation of - 10° 30′, which decreased to – 7° 55′ after hydrolysis. Charabot and Chiris invariably find rose water acid, which tends to confirm this hypothesis.

Phenyl ethyl alcohol has recently been shown to be a normal constituent of otto of rose, but it appears to be mostly, if not entirely lost or destroyed by the Bulgarian method of distillation. Nerol is also present in small amount as well as, probably, farnesol, a sesquiterpene alcohol $C_{15}H_{26}O$, present in oil of cassie flowers. Eugenol and nonylic aldehyde are also probably present in traces. It is possible that the method of distillation by steam vacuum stills in Bulgaria causes the

phenyl ethyl alcohol to be preserved in the otto, and less stearoptene to be brought over. It will probably be necessary to fix fresh standards for this steam-distilled otto as soon as more stills are working in Bulgaria. At present it is only possible to say that such otto appears to have a much higher specific gravity and refractive index than ordinary otto, and to contain phenol ethyl alcohol.

Schimmel & Co. have recently suggested the following figures for Bulgarian rose oil: $d_{15^\circ}^{25^\circ}$ 0·849 to 0·862, rarely up to 0·863; a_d − 1° 30′ to − 3°; $n_{d_{250}}$ 1·452 to 1·464; congealing point + 19° to + 23·5°; acid number 0·5 to 3; ester number 8 to 16; total geraniol (geraniol plus citronellol) 66 to 74 per cent., exceptionally up to 76 per cent.; citronellol 26 to 37 per cent., generally 30 to 33 per cent.

The citronellol determination is carried out by formylating; they take for 1 vol. oil 2 vols. 100 per cent. formic acid, and heat the mixture for one hour in a reflux condenser; for the rest the process is the same as in acetylating.

It must be admitted that the sense of smell is one of the most useful criteria of the purity of this oil, and, on account of the high price and wholesale adulteration, it is imperative that the oil should be purchased through a reliable source. Its sole employment is for the purposes of perfumery; its employment in pharmacy being merely to scent various preparations.

Oil of Bitter Almonds.—The true bitter almond oil is obtained by distilling the seeds (almonds) of *Amygdalus communis var. amara* with water after the fixed oil has been extracted by expression. The kernels of the apricot and peach yield essential oils practically identical with that from the almond, and the greater part of the bitter almond oil of commerce, especially the foreign oil, is obtained from the former (*Prunus armeniaca*). The following remarks may be taken as generally applicable to all three oils :—

Bitter almond oil does not exist as such ready formed in the seeds (almonds, kernels). It results from the action of water on the glucoside amygdalin, under the influence of the natural ferment emulsin, present in the seeds. The reaction taking place is expressed by the following equation :—[1]

$$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + 2C_6H_{12}O_6 + HCN.$$

Amygdalin. Benzaldehyde. Dextrose.

Amygdalin, taking up two molecules of water, yields benzaldehyde, dextrose and hydrocyanic acid. Amygdalin is a crystalline body, without any smell of the bitter almond and does not yield the oil except under the influence of a hydrolytic agent, such as the natural ferment emulsin, or by boiling with dilute acids. The action of the ferment is destroyed by heat or by warm alcohol. Hence if dried and powdered bitter almonds are shaken with boiling water and distilled, no oil is obtained. After the fixed oil has been expressed the press-cakes are ground up and soaked for about twenty-four hours in twice their weight of water, to which a quantity of salt is usually added. The whole is then subjected to distillation. Some trouble, however, is experienced during the process, as the large quantity of albuminoids present causes excessive frothing. To remedy this, the press-cakes are coarsely powdered and at once immersed in boiling water to coagulate the albuminoids and dissolve the amygdalin. The emulsin is, of course, rendered inactive, so that on cooling, a quantity of emulsin of the fresh cake in cold water is added to the previously treated mass. This is allowed to stand, until the emulsin will have converted the whole of the amygdalin into essential oil. The mixture is now distilled. As hydrocyanic acid is a very deadly substance, it is necessary to use great care

[1] Brannt (*Animal and Vegetable Fats and Oils*) gives the following extraordinary and erroneous reaction :—

$$2C_{20}H_{27}NO_{11} = 4C_7H_6O + 2HCN + C_6H_{12}O_6 + 4CH_2O_2 + 4H_2O.$$

Amygdalin. Benzalhchyde. Glucose. Formic Acid.

that none of the vapour is allowed to escape into the air. The distillation is effected by direct steam in most cases. The oil of almonds so obtained contains a considerable amount of hydrocyanic acid, the remainder being almost pure benzaldehyde, $C_6H_5 . COH$. The absolutely natural oil is a regular commercial article, but much is deprived of its hydrocyanic acid before being sold, and is then listed at a correspondingly high price as "Oil of Almonds (S.A.P.)" (*i.e., Sine Acid. Prussic.*). The following methods are used to deprive the oil of this poisonous constituent:—

The oil is mixed with its own volume of water and the mixture left on a water bath with red oxide of mercury, slaked lime and ferrous chloride, out of contact with the air. After all the prussic acid has been decomposed, the oil is rectified and contains no trace of prussic acid. This process was suggested by Redwood. Liebig used oxide of mercury only. Mackay prefers agitating at intervals for forty-eight hours with a mixture of lime and liquor potassæ. To detect any traces of prussic acid left in the oil, a little of it is dissolved in alcohol, and a little solution of potash and a little solution of ferrous sulphate are added. On the addition of a dilute acid, Prussian blue appears if any hydrocyanic acid is present. Benzaldehyde is very readily oxidised by the oxygen of the atmosphere to benzoic acid, so that the oil almost invariably contains traces of this body, and if kept in bottles that are not quite full the oxidation becomes more rapid, and crystals of benzoic acid are deposited. This is more especially the case when the oil has been freed from prussic acid. According to Schimmel & Co., 10 per cent. of alcohol added to the oil retards this oxidation.

Benzaldehyde is very easy to manufacture on a large scale by numerous processes, consequently artificial oil of almonds (not to be confounded with the coarse imitation oil, nitro-

benzene or mirbane oil) is now a regular commercial article, and may be obtained in various grades of purity. Although very useful for the cheaper grades of perfumery, this artificial oil does not possess the delicate odour of the natural body. To get the best results the artificial oil should be obtained free from chlorine, which is usually present in the cheap commercial article. The usual methods of preparing benzaldehyde are by heating two parts of benzyl chloride with three parts of lead or copper nitrate and ten parts of water in a current of carbonic anhydride for some hours under a reflux condenser; or some similar condensing process. Half the liquid is then distilled off and the oil separated. Or benzal chloride $C_6 . H_5 . CHCl_2$ is heated in an iron vessel with lime or soda, under pressure. Pure benzaldehyde is a colourless mobile liquid, of specific gravity 1·050, boiling at 179°. It is more soluble in water than most essential oils.

Natural almond oil is, in the crude state, a yellowish liquid, but is white when rectified, of specific gravity 1·045 to 1·070, but usually from 1·045 to 1·055. It is optically inactive. Its refractive index is about 1·545 or, if free from prussic acid, 1·550. It is often adulterated with artificial benzaldehyde, and if the purest variety be used it is impossible, within certain limits, to detect it, except, possibly, by the nose. If the cheaper variety has been used, chlorine compounds will be present and may be detected as follows. A piece of filter paper is saturated with the oil and placed on a small porcelain dish standing in a larger one. A large beaker whose sides are moistened with distilled water is stood over the smaller dish, the paper having been set alight.

The gases generated by the combustion are, to a certain extent, absorbed by the water on the sides of the beaker, which is rinsed out with a little more distilled water. The liquid is filtered, and one drop of nitric acid and a few drops of solution of silver nitrate are added to the filtrate; the

formation of insoluble silver chloride is strong evidence that artificial benzaldehyde is present.

In addition to benzaldehyde (and 4 to 8 per cent. of hydrocyanic acid) oil of almonds contains phenyl-hydroxy-acetonitrile (the nitrile of mandelic acid), $C_6H_5CH(OH)CN$. In some specimens of oil, probably those which have been prepared at a high temperature, benzoin has been found. This body has the formula $C_6H_5CH(OH)CO.C_6H_5$. Hydrocyanic acid may be detected by adding to water which has been well shaken with the oil ferric and ferrous chlorides or sulphates and then solution of caustic potash. On acidifying the liquid a blue-green colour or precipitate will be formed in the presence of hydrocyanic acid (ferrocyanides and ferricyanides). It may be estimated by dissolving 1 gramme of oil in 5 c.c. of alcohol, and adding 50 c.c. of water. Then add ammonio-silver nitrate solution and shake well. Acidify slightly with nitric acid, and collect, wash and dry the silver cyanide precipitated. Ignite and weigh the silver, four parts of which correspond to practically one of hydrocyanic acid.

Another adulterant, of a much grosser character, is oil of mirbane. This is the cheap almond oil substitute so largely used for perfuming common toilet soaps. Chemically it is nitrobenzene $C_6H_5NO_2$, more or less mixed with impurities, of which the most common is nitrotoluene, which sometimes itself forms the greater part of cheap nitrobenzene. Indeed, nitrotoluene in any great quantity may be regarded as an adulterant of nitrobenzene. The latter, when pure, is a yellowish liquid of specific gravity at 0° of 1·200, boiling at about 206°, and solidifying at + 2° to + 3°. It has a coarse almond-like odour, and is poisonous when taken internally, and irritating to the skin when used externally. The cheapness of artificial benzaldehyde should discourage its use in even the very cheap toilet soaps. Nitrotoluene $C_6H_4(CH_3)NO_2$ exists in three isomeric modifications, and nitroxylene

$(C_6H_3)(CH_3)_2NO_2$ in more still. These bodies are found to a considerable extent in the cheaper qualities of nitrobenzene. Consequently it is important that commercial samples should have physical characters in approximate agreement with those above quoted.

To detect the presence of this objectionable substituent in oil of almonds a little of the oil is warmed with iron filings and acetic acid. The nitrobenzene is reduced to aniline $C_6H_5NH_2$, which is distilled off and collected. To the distillate a few drops of solution of ordinary chloride of lime is added. If aniline be present the liquid yields the characteristic violet colour. Pure benzaldehyde combines with sodium bisulphite to form a crystalline compound without the characteristic almond odour. Samples adulterated with nitrobenzene, when shaken with excess of bisulphite of sodium solution, so that the benzaldehyde is entirely combined, then have the characteristic coarse nitrobenzene odour.

This oil is used in confectionery, perfumery, and, to a small extent, in medicine. The oils distilled from peach and apricot kernels are practically identical with essential oil of almonds.

Cherry Laurel Oil is distilled from the leaves of *Prunus laurocerasus*, an evergreen shrub, a native of South-eastern Europe and Asia Minor. Most of the oil is distilled in the south of Switzerland and in Italy. It is obtained also in England and Germany, together with the official cherry laurel water, by distilling the leaves in the ordinary way. The oil is optically inactive, and has a specific gravity 1·050 to 1·065. It contains benzaldehyde, prussic acid, and possibly traces of benzyl alcohol, and, indeed, differs very little from oil of bitter almonds.

Wild Cherry Bark Oil.—The bark of *Prunus virginiana* yields about ·2 per cent. of essential oil of specific gravity

about 1·050, and optically inactive. It contains benzaldehyde and prussic acid, and closely resembles oil of bitter almonds.

Oil of Meadowsweet.—This oil is obtained by distilling the herb *Spiræa Ulmaria.* It contains salicylic aldehyde $C_6H_4(OH)(COH)$, a terpene, and a camphor-like substance, traces of methyl salicylate, vanillin and heliotropin. The oil is artificially prepared by distilling salicin, the glucoside of this plant, with chromic acid. If the distillation is carried too far a little furfurol also comes over, which causes the oil to become very dark on keeping. The oil is but little used.

N. O. Rutaceæ.

Lemon Oil.—This oil, one of the most important of all the essential oils from the commercial point of view, is obtained by various processes from the fresh peel of the ordinary lemon, *Citrus limonum.* The tree is a native of India, and was introduced into Southern Europe, probably first into Spain, and thence to the South of France and Italy. There are numerous varieties and hybrids, but the ordinary lemon forming the fruit of commerce is the Genoese lemon. This is cultivated on the Mediterranean littoral, especially between Nice and Genoa, in Calabria, Sicily, Spain and Portugal, and on nearly the whole coast of Liguria. Many of the British Colonies are now cultivating this fruit, Australia for many years past having filled its own requirements for lemons; the trees are also extensively grown in New South Wales, Florida, California and Jamaica, and will, probably, shortly produce the oil in considerable quantities. The oil is obtained between the months of November and March, or April, and the processes used are the following (which have been already described in detail, *see* page 80 *et seq.*). (1) The Spugna or sponge process, by which the oil is removed from the burst oil cells of the peel by a sponge. (2) The Ecuelle

method, by which the lemons are rolled about in vessels covered with spikes and the oil collected in a receptacle in the handle of the vessel. (3) Machine processes, such as the thermo-extractor described on page 85. (4) Simple distillation. This method gives a very inferior oil, and is often applied to the peels from which all the oil obtainable by other processes has been obtained. (5) Expression in bags in ordinary presses.

The sponge method is the typical process in use in the chief lemon oil districts—Sicily and Calabria; the ecuelle method being employed chiefly in the South of France and North of Italy, and to a certain extent, of course, in the south.

The oil, though fairly constant in its characters when pure, varies according to the period of the harvest, the weather and the locality. For example, the oil obtained during the first two months of the season—November and December—is usually of the finest character, and also, possibly as a coincidence only, usually possesses the highest optical rotation.

The greater part of the oil of commerce is produced in the district of Messina, on the north-east of the island of Sicily, and the adjacent districts along the coast to the west; a considerable amount is produced in the Palermo province, and all along the east coast of the island; and a large amount also in Calabria, which is chiefly exported from Reggio. An approximate idea of the relative production of these districts is seen from the export returns during 1905, which were as follows:—

From Messina	742,567 kilos.
„ Reggio	95,319 „
„ Palermo	26,041 „
„ Catania	4,317 „

Apart from the alteration in rotatory power suggested above as coinciding with the time of the crop, although

possibly having no direct relation to the quality of the oil, it is found that the oil obtained from round about Barcelona (near the northern coast) and from the plains of Syracuse (on the south-eastern coast) possess the highest average rotations of all the oils, this figure varying from + 64° to + 65°. The following figures are found for the various districts :—

From + 57° to + 61°	. Messina and neighbourhood, Nizza di Sicilia.
„ + 61° to + 63°	. Acireale, S. Teresa di Riva, Scaletta, S. Lucia, Patti, S. Agata, S. Stefano.
„ + 63° to + 64°	. Catania, Giarre, Giardini, Acireale, Lentini.
„ + 64° to + 65°	. Barcelona, Syracusa.

Palermo oils are usually about + 57° to + 61°, and the Calabrian oils at + 59° to + 62° 30′. In the author's experience these limits are of very small value and cannot be taken as in the least degree conclusive. Cool rainy weather appears to have some effect on the optical rotation, but all one can say conclusively is that the average rotation observed during one season's crop is sometimes 2° or 3° higher or lower than that of the preceding year. The Palermo oil and the Messina oil differ somewhat in their odour, etc., so that a trained nose can discriminate between them. This difference has been, to a certain extent at all events, explained by Umney and Swinton (*vide infra*).

The well-defined constituents of lemon oil are the terpenes limonene, laevo-pinene, camphene and the sesquiterpene limene; limonene forming about 90 per cent. of the oil. The oxygenated bodies fuming the other 10 per cent. are citral, nonyl and decyl aldehydes, geraniol and linalol and their acetic esters (the latter stated to be only present in Palermo oils and thus probably accounting for the slight difference in odour between this and Messina oils), citraptene $C_{11}H_{10}O_4$, and a stearoptene of unknown constitution.

A study, covering a *résumé* of other work on the question of citraptene (limettin) by Ernst Schmidt, appears in the

Archiv der Pharmazie (1904, 288). The early work of Brissenot, Blanchet and Sell and Mulder is referred to, as is also the analysis by Berthelot. This brings us up to the first of the recent workers, Crismer, who gave 143° to 144° as the melting point, and $C_{10}H_{10}O_4$ as the formula of the stearoptene of lemon oil. Schmidt isolated a crystalline body melting at 146° to 147° and having a blue fluorescence in alcohol solution, and he states that this body is the citraptene of Crismer, and the limettin of Tilden and Beck. Théulier had already stated that a crystalline body melting at 145° and an amorphous one melting at 76° were the chief constituents of the solid mass obtained on the distillation of lemon oil; of these citraptene is the principal.

Schmidt gives 146° to 147° as the melting point of this body, for which the name citraptene is retained. Three analyses gave the following results:—

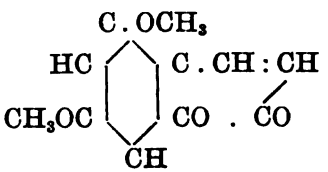
Carbon.	*Hydrogen.*	*Calculated for* $C_{11}H_{10}O_4$.	
63·92	5·04	C	63·98
63·83	5·01	H	4·85
63·82	4·75	O	31·17

This formula is in agreement with that assigned to limettin by Tilden and Beck.

Citraptene contains two methoxyl groups; when treated by Zeisel's method to remove the methyl groups, the demethylated citraptene, $C_9H_6O_4$, yields phloroglucin and acetic acid on fusion with alkali.

Citraptene has the general character of an acid anhydride, according to Schmidt, its corresponding acid being unstable and rapidly converted into a lactone.

Citraptene appears to be a di-methoxy-coumarin of the formula—



Citral with the nonyl and decyl aldehydes are perhaps the chief odour-bearing constituents and are present from 3 to 4 per cent. in the oil.

Adulteration, which was until recently very frequent, is still common. Turpentine was the regular adulterant, with, at times, the poorer quality distilled oil of lemons. But adulteration with turpentine is now so easily detected that the sophistication is frequently carried out in a more scientific manner. Mixtures with the proper specific gravity and optical rotation can easily be made up from turpentine and orange oil—the poorer qualities of the latter of course being used—and such mixtures are often used to adulterate the oil. But the most formidable adulterant from the analyst's point of view is one that has only come into vogue during the last few years, *viz.*, the terpenes obtained in manufacturing the "terpeneless" or concentrated oils of lemon and oil of orange, the latter being sometimes added to turpentine to raise the optical rotation.

The terpenes are sometimes used alone, sometimes together with a little citral obtained from lemon-grass oil. Before discussing the analysis of lemon oil, a few words on the citral content will not be out of place. It is a common custom to export oil of lemons with a guaranteed citral content, and to sell it upon that basis. In judging of the value of such a basis for the market value of the oil, the following points should be carefully noted:—

(1) The value of the oil depends on its percentage of oxygenated constituents, which are soluble in weak alcohol.

(2) The terpenes are practically odourless and insoluble, therefore valueless, for the general purposes for which lemon oil is employed.

(3) The percentage of terpeneless oil obtained by careful fractionation is an indication of the value of the oil.

It would be more rational in valuing this oil not to give

the percentage of citral which might be, in fact often is, added as lemon-grass citral, but to return the amount of terpeneless oil actually obtainable by careful fractionation. It has been found in practice that genuine oils only yield from 5 to 6 per cent. of terpeneless oil, which in the strict sense of the term are not terpeneless but contain a fair proportion of sesquiterpenes; however, such oils will not contain more than 50 per cent. of total aldehydes, and therefore the amount of citral calculated on the original oil would be about 3 per cent. No lemon oil ever contains anything like 7 per cent. of citral, which is a figure often given by Messina analysts.

Although the determination of citral has for some years past been considered by many analysts the most important factor in the valuation of this oil, it will be seen from the above remarks that it will be somewhat misleading when citral from lemon grass or *Backhousia citriodora* is added. At present there is no really accurate or reliable method for the determination of citral in lemon oil (although many have been recently suggested); this is not surprising when the small amount of aldehydes normally present is considered.

Lemon oil is apt to deteriorate on keeping. It will often become cloudy and paler in colour and develop an unpleasant odour. The traces of water dissolved in the oil, and afterwards separating out, are responsible for the turbidity, but the general deterioration is undoubtedly due to chemical change, in which the terpenes play the chief part. To keep the oil most perfectly it should be stored in bottles quite full, to avoid contact with air, and in a cool dark place. Absolute alcohol is also added to the oil for the purpose of keeping it.

Chemical and Physical constants: The specific gravity of a pure lemon oil should be between ·857 and ·862. These limits are rarely exceeded. The optical rotation taken at 20° should not be less than + 57°, and is usually between this figure and + 64°. Increase in temperature causes a slight

diminution in rotatory power, but this does not amount to more than about − 8′ or − 9′ per degree rise in the temperature of the oil. The refractive index for pure oils lies within the comparatively narrow limits of 1·4730 to 1·4750. Pure lemon oil commences to boil at 170° to 172°, and from 20 to 30 per cent. will be obtained from 172° to 174°. However, the percentage of the fractions at temperatures near to one another are so dependent on the exact form of the fractionator, that the results are not constant enough to be of much value, unless any oil distils below 170°.

To determine the purity or otherwise of lemon oil a somewhat prolonged analysis is necessary, no one constant being of much value by itself; in fact since the old crude form of adulteration by means of turpentine has been almost entirely replaced by the more scientific adulteration with terpenes (the by-product obtained in the manufacture of terpeneless oils) and a small amount of citral from lemon-grass oil, the true value of an oil can only be ascertained by means of careful fractionation.

The following scheme will however detect any adulteration :—

(1) Determine the specific gravity at 15° C.

(2) Optical rotation, a_D (100 mm. tube).

(3) Refractive index, N_D at 20° C.

(4) Fractionally distil as follows:

Introduce into a distilling flask having three bulbs blown in the neck, 100 c.c. of the oil to be tested. The receiver is an ordinary Bruhl apparatus with two vessels graduated at 10 and 80 c.c. respectively. The whole apparatus is then exhausted by means of a water pump (or other suitable means), and when a pressure of not more than 20 mm. is obtained as shown on a gauge, the distillation is commenced by gently heating the oil bath containing the flask.

The first fraction is collected in the 10 c.c. tube and the

second in the 80 c.c. flask. Directly the second fraction is collected the pressure is released, and the distillation continued by passing a current of steam into the distillation flask and collecting the oil and water into a suitable vessel. When about 200 c.c. of water have been collected, the distillation is stopped; the oil is then separated from the water and carefully measured.

The rotation and refractive index of the three fractions are then carefully determined, and further with No. 3 the aldehydes are estimated with normal sulphite of soda taking 5 c.c. as described at page 133.

Interpretation of results:—

No. 1 will indicate the addition of turpentine; there should not be a greater difference than 10° between the rotation of this and of the original oil, 7° to 8° being the average for normal oils.

Note.—Pinene is a natural constituent of lemon oil, but only in traces.

The refractive index will be about 2 points in the third place of decimals lower than that of the original oil. This fraction will also indicate substances of low boiling point.

Fraction 2 will indicate chiefly the addition of added terpenes, normal oils showing an *increase* of 6° to 7° rotation from the original oil, whereas with added terpenes the increase will be considerably higher and the refractive index lower.

Fraction 3 is in many respects the most important, inasmuch that it indicates the true proportion of oxygenated constituents of the oil and therefore the strength of the oil. The rotation will depend partly to the amount of oil obtained by the steam distillation which is usually between 6·5 to 7·5 c.c., the rotation being about + 2° to + 14°, but in some very rich oils the sign may be minus.

The refractive index will also have increased to nearly 1·4800 in this fraction. The aldehydic content should be in

direct ratio to the amount of the fraction, giving from 36 to 46 per cent., which, calculated on the original oil, will show from 2·5 to 3·5 per cent. These figures are fully borne out on a commercial scale of working.

The whole question as to the valuation of lemon oil is one that requires great discrimination and discretion. As to the crops and climatic conditions during harvesting, it is unsafe to lay down any too hard and fast rules, but the method above given will show, in the hands of a careful observer, any gross adulteration. With regard to the low citral percentage found by this method (as compared to the hitherto 7 per cent. standard) the amount is quite compatible with that found in practice, and many series of determinations have failed to show as much as 1 per cent. of aldehydes in the 90 per cent. of terpenes distilled over.

With regard to the determination of citral and other aldehydes, as stated above, there is no satisfactory direct method, but the following have been used:—

(1) The most general method is by shaking a known volume of oil with a hot saturated solution of bisulphite of soda and measuring the unabsorbed oil. The reaction is probably as follows:—

$$C_9H_{15}CHO + NaHSO_3 = C_9H_{15}CH\begin{matrix}OH\\SO_3Na.\end{matrix}$$

The objection to this method is the use of a strongly acid solution which is liable to decompose some of the delicate constituents, forming resins and giving flocculent matter which obscures the meniscus, thus making the readings doubtful.

(2) By the formation of an oxime with hydroxylamine in alcoholic solution and estimation of the amount used, by titration of the unused hydroxylamine:—

$$C_9H_{15}CHO + H_2NOH = C_9H_{15}CH : NOH + H_2O.$$

A freshly prepared alcoholic solution of hydroxylamine-

hydrochloride is used, containing 1 gram of hydroxylamine-hydrochloride in 20 grammes of 80 per cent. alcohol. 10 to 12 c.c. of this solution are diluted to 250 c.c., and 25 to 50 c.c. are titrated for hydroxylamine in the usual manner, with N/10 sodium hydrate solution, using first methyl orange and then phenolphthalein as indicators.

A second equal amount of the strong hydroxylamine-hydrochloride solution is mixed with a weighed quantity of lemon oil, and diluted with absolute alcohol until a clear solution is obtained. After the addition of 0·5 gram of sodium bicarbonate, the mixture is introduced into a 150 c.c. flask and heated on the water bath for 45 minutes under a reflux condenser. After cooling, the product is washed into a 250 c.c. flask with distilled water, care being taken to wash out the condenser as well as the flask. After thoroughly shaking out, the watery layer is adjusted to 250 c.c., and 25 c.c. pipetted off. For a determination of the unused hydroxylamine in this, one drop of methyl orange is added and then diluted hydrochloric acid is cautiously run in from a burette until a faint rose colour is developed. The colour is then titrated back with N/10 sodium hydrate solution, phenolphthalein added, and titration continued until the development of a rose colour. The difference between the blank and the experiment will be the amount of hydroxylamine used, and the percentage may be calculated by the following formula: $C = \frac{1{\cdot}52 \times A}{G}$, where C = the percentage of aldehyde, A = number of c.c. of N/10 sodium hydrate solution used, and G = weight of oil taken. This is, probably, an excellent method if one only knows the approximate percentage of citral present. If known, the correct quantity of hydroxylamine and sodium bicarbonate can be added, when good results may be obtained. The method as

we have described it above gives good results with lemon oils. With practice very fair results may be obtained by this method.

(3) By the condensation compound formed with cyanacetic acid in alkaline solution:—

$$C_9H_{15}CHO + CH_2CN \cdot COOH = C_9H_{15}CH \cdot C\begin{matrix}CN\\COOH\end{matrix} + H_2O.$$

The procedure is as follows: 200 c.c. of the oil are concentrated to 25 c.c. in a Wurtz flask under a pressure which should not exceed 15 mm. The 175 c.c. of terpenes contain a little citral, but the quantity is so small that it may be neglected. Ten c.c. of the residue, of which the specific gravity is known, are shaken with a solution of 5 grammes cyanacetic acid and 5 grammes ordinary KOH in 30 c.c. water in a small absorption flask with a long graduated neck, and the non-absorbed residue read off as usual. (The specific gravity of citral is so near that of the concentrated oil used that it may be taken as identical.)

It is most important to use freshly prepared cyanacetic acid to obtain good results by this method.

(4) By the formation of a soluble sulphonic acid with sodium sulphite using phenolphthalein as an indicator:—

$$C_9H_{15}CHO + 2\ Na_2SO_3 + 2\ H_2O$$
$$= C_9H_{17}\ (NaSO_3)_2COH + 2\ NaOH$$

Professor Tiemann, in his elaborate work on the aldehydes of lemon-grass oils has, among other important reactions, shown that if citral be agitated with a neutral solution of sodium sulphite, a sodium salt of the sulphonic acid results, as shown by the above formula. By taking advantage of the sodium hydrate formed by this reaction, phenolphthalein is used as an indicator to show when all the citral has been combined; and the fact that the above sodium salt is quite soluble, has made the estimation of citral fairly accurate and

simple. The procedure is as follows: A saturated solution of sodium sulphite is prepared. To 50 c.c. of such solution 25 c.c. of the oil are added, and two drops of an alcoholic solution of phenolphthalein. The whole is then heated on a water bath to nearly boiling point, constantly shaking. A deep red colour appears almost at once, which shows that the action has commenced. A few drops of sulphurous acid are then cautiously added, and this is continued until no further colour is produced after a further addition of SO_2. The oil is then measured as described in the first method. The obvious advantage of this method is that the end of the reaction may be ascertained to a certainty, while the above bisulphite method depends on the continual shaking for a period of not less than one hour.

A modification of the method has been suggested by titrating with standard acid the sodium hydrate formed.

(5) By reducing citral with metallic sodium when geraniol is formed, which may be acetylated and the acetylated oil saponified. This method it need hardly be said is open to grave objections and is never employed now.

E. Mackay Chace (*Journ. Am. Chem. Soc.*, 28, 1472) describes a method for the estimation of citral, the results of which are more exact in the case of mixtures made up artificially than when applied to oil of lemon. This method depends on the property which magenta-sulphurous acid possesses of giving, in presence of aldehydes, a red coloration the intensity of which depends exactly on the quantity of aldehyde. The estimation is then carried out by comparison with solutions of aldehyde of known strength.

The solution of magenta-sulphurous acid is prepared as follows: 0·5 gram of magenta is dissolved in 100 c.c. of water and a solution containing 16 grammes of sulphur dioxide is then added. The liquid is allowed to stand until it is decolorised and its volume is made up to a litre with water.

Such a solution cannot be kept longer than two or three days.

Secondly, alcohol of 95 per cent. strength must be prepared absolutely free from aldehyde. For this purpose the alcohol is kept for several days in contact with a caustic alkali, it is then distilled and the distillate is boiled under a reflux condenser for a few hours with meta-phenylenediamine hydrochloride (25 grammes of the hydrochloride per litre). The alcohol is then separated by distillation and made up to the desired concentration.

Lastly, a 0·1 per cent. solution of citral in 50 per cent. alcohol is prepared.

These solutions are made up at a temperature of 15° C. and all the operations are carried out at this temperature. It is particularly recommended that a higher temperature be avoided.

Two grammes of each of the essential oils to be examined are diluted to 100 c.c. with the alcohol free from aldehyde. Four c.c. of each of the solutions are introduced into cylinders of identical dimensions, 20 c.c. of alcohol free from aldehyde are added, then 20 c.c. of magenta-sulphurous acid and the volume is made up to 50 c.c. with alcohol. After thoroughly mixing, the solutions are placed in a water bath at 15° C., and compared in regard to their colours with the necessary standards. An error of 1 per cent., however, may be made in this determination.[1]

The oil freed from its terpenes by fractional distillation or other suitable means has of recent years become very popular, which is not surprising when its easy solubility and good keeping properties are considered. The specific gravity lies between 895° to 900°, optical rotation – 7° to – 9°, refractive index 1·4810 to 1·4822. Total aldehydes between 40 per cent.

[1] The author is much indebted to Mr. H. E. Burgess for a considerable amount of information in regard to the oils of the *Rutaceæ*.

and 50 per cent. It is soluble in two parts 80 per cent. alcohol by volume.

The above class of oils are not terpeneless in the strict sense of the term inasmuch as they contain sesquiterpenes. Oils are now prepared free from sesquiterpenes. They are much more soluble and have a very fine aroma, and are sold as sesquiterpeneless oil.

Oil of Orange.—There are two varieties of ordinary orange oil in commerce, almost identical in composition and properties, but with odours and flavours somewhat different. These are the bitter and sweet orange oils, obtained in the same manner and in the same localities as oil of lemon, from the peel of *Citrus bigaradia* and *Citrus aurantium* respectively. With regard to the origin of the trees, Professor Sadebeck (*Plant Cultivation in the German Colonies, and their Products*) says: "The orange tree is probably indigenous to South-eastern Asia (Cochin China), and thence has spread to the Sunda Islands, further India, Persia, Arabia, Syria, North Africa and Southern Europe. Towards the end of the ninth century of the Christian era, it appeared in Arabia, and since A.D. 1002 in Sicily." An oil is prepared by distillation in Jamaica, but it is much inferior in every respect to the expressed oil.

Considerable parcels of best Indian oil have recently been placed on the London market, the examination of which shows this to be equal if not superior to Sicilian oil.

The oil is, in general, produced in the same localities as oil of lemon, but the greater part of it is obtained from Calabria and Messina. The two oils are, chemically, practically indistinguishable, and much of the "bitter" oil, which commands a higher price, is in reality a mixture of the two oils.

The oil consists principally of *d*-limonene (up to 95 per cent.). The following bodies have also been identified, decyl-aldehyde, *d*-terpineol, *d*-linalool, methyl-anthranilate and

citraptene. The occurrence of citral as a constituent of natural oils is somewhat doubtful.

The total amount of oxygenated constituents of the oil is, however, very small, probably not more than 3 per cent., whilst the decyl-aldehyde and methyl-anthranilate play an important part as odour-bearing constituents.

The specific gravity lies between ·848 to ·852; anything outside these figures should be looked upon with suspicion. The addition of turpentine or lemon oil will be indicated on fractional distillation.

The rotatory power of sweet orange oil should be between 96° to 99°, the refractive index 1·4725 to 1·4735.

Examination of the Oil.—The method given for lemon oil will be found equally serviceable to detect adulteration of this oil. The two chief adulterants are lemon oil and orange terpene (auranciene), of which the latter is by far the most difficult to detect even if added in considerable quantities. Such sophistication is very prevalent in Sicily. It is a well-known fact that orange terpenes command nearly as high a price as the oil itself. Owing to the very small percentage of oxygenated constituents in the oil, these terpenes may be added with impunity without much fear of detection.

Turpentine, another adulterant, is seldom employed now. The rotation of the oil itself and distillation of the first 10 per cent. at once revealing its presence.

The distillation figures show that for the first 10 c.c. distilled, the rotation will be slightly higher than the original oil, whereas if lemon oil or turpentine is present it would be considerably lower.

The refractive index is always lower than for the same fraction of lemon oil.

The rotation of the next 80 c.c. will have increased from 3° to 4°, and if terpenes are present may be as much as 6° from the original oil.

The refractive index will increase slightly, about 2 to 3 points in fourth place of decimals; by the addition of orange terpenes an addition of lemon oil would make the increase greater.

The last fraction indicates the true value of the oil, about 8 c.c. should be obtained, having a rotation + 82° to + 88°.

The refractive index of the last fraction is lower than that of both the 10 and 80 fraction, or the original oil, lying between 1·4715 and 1·4725. This low figure is due to the decyl aldehyde. The aldehydic content, chiefly decyl-aldehyde, will be about 12 per cent., which calculated to the original oil gives from 0·7 to 0·9 per cent.

Bitter Orange Oil.—The same remarks in general apply to the bitter oil as to the sweet, except that the rotation very often is 4° to 6° lower.

Oils from the following sources have also been examined:—

		Specific Gravity.	*Rotation.*
West Indian	Sweet	·8475	+ 98·30
	Bitter	·8504	+ 97·30
Dominica	Sweet	·855	+ 96·58
	Bitter	·853	+ 95·57
Florida, U.S.A.	Sour	·856	+ 94·15
	Bitter-sweet	·856	+ 96·25

The distilled oil of orange owes its inferiority to the effects of heat and steam on the oxygenated constituents, which are of an exceedingly delicate nature.

Terpeneless Orange Oil.—As will be seen from the above orange oil contains an extremely small amount of oxygenated constituents and therefore the concentrated oil commands a high price. Extreme care is necessary for its manufacture, owing to the extreme solubility of the aldehydes and delicate nature of its esters.

In addition to the ordinary orange oil, oils of Mandarin and Tangerine oranges are articles of commerce. Occasionally

these are met with in a state of purity, but the average sample consists chiefly of ordinary orange oil with a little of the more sweet-scented variety. Mandarin oil is, according to Luca, derived from the fruit of *Citrus bigaradia simensis* and *Citrus bigaradia myrtifolia*. Sawyer calls it *Citrus nobilis*, and Schimmel & Co. describe it as *Citrus madurensis*. It is cultivated largely in China, and the fruit is usually presented to the mandarins, whence its name. It is also cultivated in Malta and the Azores. Luca, so long ago as 1857, investigated the oil (*Comptes Rendus*, 23rd November, 1857) and described it as a liquid of specific gravity ·852 at 10°, boiling at 178°, and having the composition of a terpene. However, it is now certain that the oil contains citral, probably citronellal, and about 1 per cent. of the ester, methyl-anthranilate, discovered in ordinary orange oil by the author. The specific gravity of this oil is usually rather higher than that of ordinary orange oil, generally falling between ·852 and ·858. The optical rotation, however, is considerably lower, from + 65° to + 75°.

Oil from Tangerine oranges very closely resembles the above described and is possibly identical with it. The author has examined an undoubtedly pure sample, which had the following properties. Specific gravity, ·8589; optical rotation, + 70° 47′. On exposure to very low temperatures the oil deposited beautiful yellow crystals, which retained their colour after recrystallisation from alcohol.

Oil of Petit-grain.—The original oil of petit-grain was obtained by the distillation of the small unripe orange berry, which, according to Pereira, rapidly underwent decomposition. The petit-grain oil of to-day, however, is distilled from the leaves and young shoots of the bitter and the sweet orange, the former commanding the higher price. According to Sawyer, citrons are usually grafted on to orange stocks, and these stocks during the summer put forth shoots, which

are allowed to attain the length of a few feet. They are then pruned off, cut into bundles, and sent to the distiller. The finest oil, as indicated above, is obtained from *Citrus bigaradia*. The best quality oil comes from the south of France, and also from Algeria and the south of Spain. A much less expensive, but still a fine product, comes from Paraguay.

Pure petit-grain oil has a specific gravity ·885 to ·900, and is either laevo-rotary to − 2° (European) or dextro-rotary to + 4° (South American). It is easily soluble in twice its volume of 80 per cent. alcohol. It contains a high proportion of esters, but as this figure is very variable no limits can well be fixed. Calculated as linalyl acetate, the percentage varies from 50 to 85 per cent., usually about 55 to 60 per cent. The refractive index is about 1·4650.

The well-ascertained constituents of the oil are the terpene limonene, linalol, linalyl acetate, geraniol, geranyl acetate, a sesquiterpene, and a stearoptene not yet examined. The oil distilled exclusively from the leaves and buds is, according to Charabot and Pillet, invariably laevo-rotary, and contains a very small quantity of limonene, whereas the South American oil appears to owe its dextro-rotation to a larger percentage of limonene, which may be due to an admixture of small fruits with the distilling material.

Schimmel & Co. have examined an oil distilled from the corresponding parts of the lemon tree, which was termed by its makers "Petit-grain citronnier". The odour resembles that of petit-grain oil, with a secondary odour of lemon. Its specific gravity was ·869, optical rotation + 34° 11′, and it was far less soluble in alcohol than ordinary petit-grain oil. Citral was detected in it. This was probably mixed with ordinary lemon oil.

An oil distilled from the unripe orange fruits, analogous

to the old-fashioned petit-grain oil, is manufactured and offered under the name of "oil of orange peas". Its specific gravity is about ·852 to ·854 and its optical rotation + 75°. It is intermediate in composition between orange oil and neroli oil. It contains methyl-anthranilate and also traces of a pyrrol compound. Petit-grain oil is frequently adulterated, chiefly with turpentine, but it is now easy to get pure oil by careful buying. The oil is used extensively in perfumery, especially in the manufacture of *Eau de Cologne*, and is also employed to a considerable extent to adulterate neroli oil with.

Jeancard and Satie give the following figures for the "petit-grain" oils of lemon, orange and mandarin :—

	Sp. gr.	*Rotation.*	*Esters.*
Lemon Petit-grain . .	0·8768	+18° 20′	12·25 %
Bitter Orange Petit-grain .	0·886-0·895	−2° 40′ to −5°	47-68 %
Mandarin Petit-grain . .	0·8768	+6° 14′	45 %

Umney and Bennet have examined a Buenos Ayres oil resembling ordinary South American petit-grain oil but having more free alcohols and less esters than those oils. Pinene, dipentene, furfural, geraniol, linalol and geranyl acetate were found to be present. Its specific gravity was 0·887, optical rotation + 2°, esters 36·5 per cent., and free alcohols as geraniol 38·4 per cent.

Neroli Oil.—This oil is distilled from the fresh flowers of the bitter and the sweet orange. The former, which is the more valuable, is known as "Oil of Neroli, Bigarade" (which is ordinary neroli oil), the latter as "Oil of Neroli, Portugal". The greater part of the neroli oil of commerce is distilled in the south of France, one of the chief centres being Vallaurie. The yield of oil varies greatly according to the time of the season when the flowers are collected. The gathering of the flowers commences about the last week in April and continues

till the last week in May, or possibly a little later. The early gathered flowers yield about half a gramme of oil per kilo, whilst those gathered late in May yield double this quantity. The petals are separated from the sepals and covered with water in the still, and the contents heated by means of coils of superheated steam. The oil coming over is separated, and the water is sold as orange flower water.

Pure normal neroli oil has a specific gravity ·870 to ·880, and is always dextro-rotary, usually about + 4°, but sometimes much higher. On account of the regular adulteration of this oil with both kinds of orange oil, it is probable that rotations of + 20° and higher, which have been recorded, are not at all representative of pure oils; however, it is not easy to fix any definite limits. Again, although no definite limits can be fixed for the ester content, this usually falls between 7 and 20 per cent., calculated as linalyl acetate, and high ester contents should be regarded with great suspicion, as indicative of adulteration with petit-grain oil.

Neroli oil contains limonene, linalol, linalyl acetate, geraniol and one or more paraffin hydrocarbons. None of these bodies, however, are characteristic of the odour of neroli, nor is any one of them responsible for the characteristic fluorescence of the oil. Ernst and Hugo Erdmann (*Berichte*, 1899, p. 1213) have examined the oil, and found that the portion which distils about 115° at a pressure of 10 mm. leaves on saponification a crystalline acid of melting point about 140°. This acid was completely identified as anthranilic acid (*o*-amidobenzoic acid), and it occurs in the oil as its methyl ester. The pure body, methyl-*o*-amidobenzoate, is an oil solidifying at low temperatures in crystals, melting at 24·5° and boiling at 127° at 11 mm. Its specific gravity is 1·163 at 26°. It is easily soluble in dilute mineral acids (on account of its basic character), alcohol or ether, and yields

a crystalline hydrochloride. It is strongly fluorescent and has a powerful neroli odour. This body must, therefore, be regarded as one of the odour-bearers of oil of neroli, and artificial neroli oils are now quite easy to prepare. In regard to this discovery, Messrs. Schimmel & Co. claim that they had long known it, and made an artificial oil of neroli oil containing this ester. The crystalline body sold as "nerolin" is β-naphtol-methyl ether. Whether this occurs or not in the natural oil is uncertain.

The constituents of this oil, then, so far identified, are as follows: The terpenes limonene (probably in both optically active forms), laevo-pinene, laevo-camphene (?) and dipentene. There are also present the alcohols geraniol, linalol, nerol, dextro-terpineol, nerolidol (a sesquiterpene alcohol not hitherto found in any other oil except perhaps petit-grain oil), and possibly phenyl-ethyl alcohol. Decylic aldehyde is present in small amount. The esters present are chiefly the acetates of geraniol, linalol and nerol. There are traces of esters of phenyl acetic acid, and traces of benzoic, acetic and palmitic acids. Indol and a paraffin are present, and the characteristic fluorescent body, methyl-anthranilate. Schimmel & Co. have found in the oil obtained by the extraction of the fresh flowers with petroleum, and extracting the petroleum extract with alcohol, traces of phenyl aceto-nitrile and a crystalline body melting at 158°, a ketone with a jasmine-like odour, possibly identical with jasmone, and a high boiling sesquiterpene alcohol (nerolidol ?), with traces of a base apparently belonging to the nicotine series.

Schimmel & Co. have distilled a parcel of fresh flowers which they received preserved in salt, and used two methods of preparing the oil. The first portion was distilled with water and the separated oil collected. The water was then redistilled several times and the whole of the oil obtained was

mixed together. The second portion was distilled and the water not further treated. In both cases the oil had a specific gravity of over ·870, and both were laevo-rotary (– 0° 52′ and – 0° 40′), whereas French distillates are dextro-rotary. The refractive index is about 1·4750.

Umney and Bennett have examined a Chinese neroli oil derived from *Citrus triptera*. It had a specific gravity 0·850 and optical rotation + 35°. It contained 4·8 per cent. of esters calculated as linalyl acetate, and 21 per cent. of free alcohols as linalol. It contained much limonene, camphene, linalyl acetate, methyl-anthranilate and a paraffin.

A Spanish neroli examined by Schimmel gave the following results :—

	Bigarade (*Bitter*).	"*Portugal*" (*Sweet Orange*).
Specific gravity . . .	0·871	0·857
Optical rotation . . .	+ 10° 54′	+ 42° 47′
Acid value	1·37	1·6
Ester value	37·67	6·86
Methyl anthranilate . .	0·5 per cent.	0·3 per cent.

It is here convenient to again mention the so-called orange pea oil examined by the author. It is distilled from the unripe dried fruits, and would therefore be expected to have properties intermediate between those of orange and neroli oil. Such was found to be the case. It had a specific gravity 0·862, an optical rotation + 72°, and contains traces of methyl-anthranilate. It contains less esters and more terpenes than neroli oil.

The following table of oils distilled in 1904 was supplied by Jean Gras to Schimmel & Co. :—

Date of Manufacture.	Yield per cent.	Specific Gravity at 15° C.	Optical Rotation l=100 mm. t=20°.	Saponification number.	Solubility in Alcohol of 80 % at 22°.
May 11	0·65	0·874	} +1° 31′	43	{ 1 vol. in 1 vol. alcohol, insoluble when more alcohol was added
,, 12	0·80	0·874			
,, 13	0·89	0·874	+1° 45′	45	1 vol. in 1·5 vol. alcohol, insoluble when more alcohol was added
,, 14	0·81	0·875	+2° 8′	46	insoluble
,, 15	0·83	0·874	+1° 32′	45	do.
,, 16	0·78	0·874	} +1° 33′	47	do.
,, 17	0·87	0·874			
,, 18	0·77	0·875	+2° 8′	53	do.
,, 19	0·77	0·875	+1° 45′	56	do.
,, 20	0·77	0·875	+2° 20′	45	do.
,, 21	0·87	0·875	+2° 21′	47	1 vol. in 1 vol. alcohol, insoluble when more alcohol was added
,, 22	0·90	0·876	+2° 21′	46	1 vol. in 1·2 vol. alcohol, insoluble when more alcohol was added
,, 23	1·00	0·875	+2° 30′	43	do.
,, 24	1·03	0·874	+2° 44′	45	1 vol. in 1 vol. alcohol, insoluble when more alcohol was added
,, 25	1·06	0·874	+3° 5′	46	do.
,, 26	1·07	0·874	+3° 8′	44	do.
,, 27	1·07	0·874	+3° 30′	45	do.
,, 28	1·02	0·874	+3° 12′	47	do.
,, 29	1·11	0·874	+3° 31′	48	do.
,, 30	1·15	0·874	+3° 48′	50	1 vol. in 1. vol. and in every proportion
,, 31	0·91	0·874	+2° 51′	48	do.
June 2	0·80	0·875	+4° 20′	49	do.
Total Quantity	0·97	0·875	+2° 50′	47	1 vol. in 1 vol. alcohol, insoluble when more alcohol was added

A. Hesse and O. Zeitschel have given some details of experiments made for the determination of methyl-anthranilate. The method is based upon the property of this ester (first mentioned by H. Walbaum) of forming with sulphuric acid a sulphate which is dissolved with difficulty in ether. According to Hesse and Zeitschel it is possible to determine the content of methyl-anthranilate in essential oils, by dissolving in ether the oil to be experimented upon; it is then cooled and mixed with a solution of sulphuric acid in ether, when the anthranilate is precipitated as sulphate. The salt thus obtained is then dissolved in water, and the quantity of

the ester contained in it is determined by titration. The analyses quoted by the authors show that this method gives good results. According to them oil of orange flowers contains 0·6 per cent. of methyl-anthranilate. Freundler (*Bull. Soc. Chim.*, 1904, 882) has published the results of his researches on the derivatives of this important body. He finds that a crystalline picrate is easily obtained by warming an alcoholic solution of the two components. It melts at 104°, and has the formula $C_{14}H_{12}N_4O_9$. The great solubility of this compound is against its being employed as a means of characterising the methyl-anthranilate. But by heating in a water bath equimolecular quantities of phenyl-isosulphocyanate and methyl-anthranilate, the mass eventually solidifies completely. The reaction product melts at above 300°, and is a thioquinazoline. This body serves well to identify small quantities of methyl-anthranilate, which can be extracted from the oil in which it occurs by sodium carbonate, and the ester extracted from the aqueous solution by ether, which is evaporated, and the residue heated on a water bath with the isocyanate and some alcoholic potash.

Bergamot Oil.—This oil is obtained from the fresh peel of the fruit of *Citrus bergamia*, the ordinary bergamot. The chief centre of the industry is Southern Calabria, which is practically the only province in which the tree is cultivated, extensive plantations being situated at, and in the neighbourhoods of, Reggio, Melito, Gallico, Arangea, Sancta Catarina, S. Lorenzo, Palizzi, Staiti, etc. Almost all the oil is expressed by machines, but as these are usually adjusted for globular fruits, any that have the oblong lemon shape are treated by hand. Hand-pressed oil is, however, rarely met with in commerce. The trees are best grown on well-irrigated, low-lying lands, and are frequently cultivated amongst the lemon and orange trees. The fruit is gathered in the months of November and December and the first

week or two in January, when the manufacturing season is over. The resulting oil is of a green colour, due to the presence of chlorophyll (not to the presence of copper, as sometimes stated).

The following substances have been found in bergamot oil: octylene, the terpenes pinene, camphene, limonene, dipentene; the sesquiterpene limene, the alcohol linalol and its acetic ester linalyl acetate; a stearoptene, bergaptene, melting point 188°, a solid body of melting point 56° and traces of free acetic acid.

Linalyl acetate is, however, the active constituent, and to this substance bergamot oil owes its characteristic odour. It is present to the extent of from 30 to 40 per cent.; the lower figure must be looked on with suspicion unless the oil be derived from unripe fruit at the early part of the manufacturing season.

Pure bergamot oil has a specific gravity of ·882 to ·886 and an optical rotation of + 8° to + 22°, rarely exceeding 18°. Some samples are sufficiently light-coloured to allow their rotation to be observed in a 100 mm. tube, but usually a shorter tube must be used and the rotation calculated; refractive index, 1·4654 to 1·4660. The oil leaves a residue when evaporated on the water bath, which amounts to 4 to 6 per cent. in unadulterated oils. The ester is estimated by a quantitative saponification in the ordinary way, and should yield a result equivalent to at least 35 per cent. calculated as linalyl acetate $C_{10}H_{17}O \cdot OC \cdot CH_3$, although pure samples occasionally contain a little less than this. As the fixed residue obtained on evaporating the oil contains some saponifiable matter, it has been suggested that this also should be quantitatively saponified and the result deducted from the original saponification figure. But as it is not clear what changes occur during the evaporation, it is preferable to give the results for comparative purposes, on the direct saponification figure, and return the

same as linalyl acetate. Pure oils are soluble in half their volume of 90 per cent. alcohol, and usually in twice their volume of 80 per cent. alcohol. In the event, however, of an oil not being entirely soluble in the latter case, as some pure oils are not, the examination of the fixed residue should never be omitted, as any fatty oil, which would decrease the solubility, would be found in the residue, and any excess over 6 per cent. may be regarded as adulteration. A good judgment can be formed on these figures, and, within limits, the value of the oil may be regarded as dependent on its ester percentage.

Rectification by steam, instead of improving, certainly deteriorates bergamot oil. This is due to the fact that the ester is decomposed, so that the percentage of this body falls to 15 or 20 per cent., and the percentage of free linalol increases correspondingly. Of course, rectification removes the green colour, but apart from that, there is nothing to repay the extra trouble and cost.

Amongst the adulterants of bergamot oil, are turpentine, lemon, orange, and fatty oils. The addition of the three first named decrease the specific gravity, solubility and ester percentage; lemon or orange oils raise the rotation. Fatty oils decrease the solubility and increase the residue obtained on evaporation. In addition to these, oil of bergamot of an inferior character is obtained by rasping the peel of the injured small fruit which falls from the tree, and mixing the pulp with water, whereby the oil separates. The residual pulp both of this, and the residue obtained after expressing the oil in the ordinary way from normal fruit, is distilled, and the distilled oil of inferior odour is frequently mixed with the normal oil. This distilled oil is characterised by a low ester percentage, exactly as in the case of rectified oils.

Bergamot oil is employed exclusively in perfumery. Artificially prepared linalyl acetate is an article of commerce,

but its price is far higher than that of pure bergamot oil, and its odour, in the author's opinion, much inferior.

Other adulterants to bring up the apparent ester value have been used, such as pinene hydrochloride, of which as much as 10 per cent. may be added without materially disturbing the physical constants. It may be detected by evaporating the alcoholic solution after saponification to dryness in a platinum dish, igniting and taking up the residue with water and testing with silver nitrate, when a white precipitate, soluble in ammonia, will reveal its presence on burning some of the oil on a filter paper as directed for detection of chlorine in almond oil.

Also the acetic esters of glycerine (acetines) have been found, and when present glycerine will be found in the alcoholic solution on evaporation. Terpinyl acetate is also used as an adulterant.

Oil of Limes.—There are two distinct oils found in commerce, the one, hand-pressed oil obtained from the *Citrus limetta* (Italian), the other, distilled oil from *Citrus medica var. acida* (West Indian). Expressed oil is prepared from the fruit in December and January. In the south-west of Italy the tree is known as *limoncello di Spagna.* The oil somewhat resembles lemon oil but with a much richer odour, somewhat recalling the odour of bergamot. It contains pinene, limonene and probably dipentene, linalol, linalyl acetate and citral (6 to 10 per cent.), limettin, melting point 147°, and a stearoptene; it has the following constants: specific gravity ·875 to ·885, optical rotation + 35° to + 40°, refractive index 1·4840 to 1·4850. Adulterants such as lemon oil and terpenes are frequently used and may be detected by distillation tests as given for lemon and orange oils. Distilled oil of limes, the usual oil of commerce, is obtained from Jamaica, Dominica and Tahiti, but chiefly from the island of Montserrat, the harvest lasting from September to January.

The oil is really a by-product obtained by distillation during the concentration of the lime juice, and the peculiar odour is due to the partial decomposition of the oxygenated constituents. Citral decomposes into cymene when boiled with dilute acids. It contains pinene, limonene, cymene, dipentene, limene and l-terpineol, melting point 35°, and another alcohol having a strong lime-like odour forming a urethane, melting point 131°, but not yet identified. Distilled lime oil has the following constants: specific gravity ·856 to ·864, optical rotation + 40°, refractive index about 1·4700.

Oil of Shaddock.—The shaddock is the fruit of *Citrus decumanum.* It is a large fruit, native to China and Japan, and introduced into the West Indies by Captain Shaddock, whence its name. The oil, which is not known to any extent in commerce, has a specific gravity of about ·860 and an optical rotation of + 90° to + 95°. It is a typical *Citrus* oil, containing much limonene, but its constituents have not yet been carefully examined.

Citron Oil.—This oil is expressed from the fresh peel of the fruit of the true *Citrus medica*, the ordinary citron, a native of the Himalayas, which was cultivated by the Aryans from very early times. In France the fruit is known as a "cédrat"—the French "citron" being our lemon. Consequently "essence de citrons" must not be confused with citron oil. The tree flourishes in the south of Europe, particularly in Italy, the fruit sometimes weighing from 10 to 14 lb. This oil, which is seldom met with pure, should have the following constants: specific gravity ·851 to ·854, rotation + 79° to 82°, refractive index about 1·4750. It contains chiefly limonene, dipentene, citral and a crystalline body, melting point 145°. The usual adulterants are lemon and orange oils and their terpenes. The odour of this oil is very little superior to that of good lemon oil, whereas the price demanded, about ten times more, does not justify its

extensive use in commerce. The adulterants above stated will be indicated by the fractional distillation test as set forth for lemon and orange oils.

Oil of Rue.—The herb *Ruta graveolens* yields an essential oil characterised by its extremely low specific gravity. The oil is of a pale yellow colour and characteristic odour, and consists almost entirely (at least 90 per cent.) of methyl nonyl-ketone, $CH_3 . CO . C_9H_{19}$. The specific gravity of the oil varies from ·830 to ·840, and it is always slightly dextrorotary, from 0° to + 2° 30′. When exposed to the action of a freezing mixture the oil solidifies to a crystalline mass at + 9° to + 10°. It begins to boil at 215°, and is completely distilled at 232°. It should dissolve to a clear solution with from two to three volumes of 70 per cent. alcohol. The refractive index is about 1·4360. Pure methyl-nonyl-ketone is a bluish fluorescent oil melting at + 15° and boiling at 225°. Schimmel found traces of a basic substance present in the oil, which is probably the methyl ether of methyl-anthranilic acid, and which will account for the fluorescence of the oil. Van Soden has examined an Algerian oil of rue, and found it to have a specific gravity 0·842 and optical rotation − 5°. It did not solidify even at − 15°. Its principal constituent was found to be methyl-heptyl-ketone, whilst only a small quantity of methyl-nonyl-ketone was present. A German oil investigated by Houbler was found to contain both ketones, the methyl-nonyl-ketone predominating. Traces of caprylic acid and of a phenol were detected. Power and Lees have examined an oil, probably of Algerian origin, and found present a basic substance having an odour of quinoline, traces of methyl salicylate and of salicylic acid. They also found valeric acid (as esters?), laevopinene, limonene and cineol. The alcohols corresponding to the ketones were also found present. Carrette states that in Algeria two kinds of oil of rue are produced; one is distilled

from *Ruta montana* and is known as "summer oil"; the other is distilled from *Ruta bracteosa* and is known as "winter oil". The former contains methyl-nonyl-ketone and melts at + 5° to + 8°. The latter consists chiefly of methyl-heptyl-ketone and only solidifies at - 18°. The characters above given are sufficient to guard against adulteration, which, however, is frequently practised, the usual adulterant being turpentine and, more rarely, petroleum, which, however, alter the constants of the oil so much as to be very easily detected. Oil of rue is not largely employed in medicine, and has occasionally been employed for illegitimate purposes.

Oil of Buchu.—Several species of *Barosma* are known by the name *Buchu*, and from the leaves of these the oil is distilled. The chief of these are *Barosma serratifolia*, *Barosma betulina* and *Barosma crenulata*. The yield of oil is from 1 to 2 per cent. The specific gravity of the oil, which possesses a camphoraceous odour, varies from ·940 to ·945, or, occasionally, a little lower, especially in the case of the oil from the leaves of *Barosma betulina*. The refractive index is about 1·4800. Flückiger investigated the oil (*Pharm. Jour.* [3], ii., pp. 174 and 219) and stated that it consisted of two main constituents, a solid one, diosphenol, and a liquid one. The more recent researches of Kondakoff and Bialobrzeski have proved that the oil contains several constituents. These are diosphenol $C_{10}H_{16}O_2$, the chief optically inactive compound in the oil; the terpenes limonene and dipentene, and a ketone $C_{10}H_{18}O$ which is probably laevo-menthone. Diosphenol is a crystalline solid, melting at 81° and boiling at 232°. It occurs only to a very small extent in the oil distilled from the leaves of *Barosma serratifolia*, whereas that from *Barosma betulina* contains so much that crystals separate at ordinary temperature. The hydrocarbon above referred to is an optically active liquid, $[a]_d = + 60° 40'$, of specific gravity ·866, and boiling at 174° to 176°. It has an odour recalling

that of pine leaves. The ketone $C_{10}H_{18}O$ is a slightly laevo-rotary liquid boiling at 206° to 209°, of specific gravity ·902, of agreeable peppermint-like odour. Pure diosphenol can be obtained from the oil by extraction with soda solution and decomposition of the alkaline liquid with an acid, and recrystallising the crude diosphenol from a mixture of alcohol and ether. Buchu oil is often adulterated with turpentine and possibly other oils. It is used to a small extent in medicine.

Angostura Oil.—The bark of *Galipea cusparia* yields between ·5 and 2 per cent. of essential oil. The tree is found in abundance on the mountains in Venezuela, and it is especially plentiful in the country round about the Gulf of Santa Fé. The name *angostura* appears to have been given to it on account of its having been found first in the district bearing that name, situated on the Orinoco. The oil has a specific gravity ·930 to ·960, and an optical rotation of – 35° to – 50°. It has been investigated by Beckurts and his pupils. In their earlier investigations (*Arch. Pharm.*, ccxxix., p. 591) they obtained 1·5 per cent. of oil from the bark, of specific gravity ·956. More recently (*Arch. Pharm.*, ccxxxv., pp. 518, 634) they obtained the same yield of oil of specific gravity ·941 at 20°, of optical rotation – 50°. The oil decomposes partially, when distilled under ordinary pressure, with the formation of water. A small portion was obtained boiling at 160°, and having an odour resembling pinene. A small quantity of a terpene is thus probably present. The main portion of the oil, however, distils between 260° and 280°, and consists of a sesquiterpene and a sesquiterpene alcohol. The sesquiterpene, which is laevo-rotary, was originally described under the name *galipene*, but has now been shown to be identical with cadinene. The alcohol $C_{15}H_{16}O$ is termed galipol; it is a liquid of specific gravity ·927 at 20°, and is optically inactive. By

the action of dehydrating agents this body gives up water and yields cadinene. In addition to these bodies there is also present a small quantity of an inactive sesquiterpene, and traces of a crystalline stearoptene. The oil is used to a small extent, chiefly for the preparation of liqueurs, etc.

Jaborandi Oil.—The leaves of *Pilocarpus pinnatifolius* yield about 5 per cent. of an essential oil, of specific gravity about 0·865 to 0·895. Its optical rotation is about + 30°. It is soluble in two volumes of 80 per cent. alcohol. Its composition is not well known, but the terpene dipentene has been identified, and also a crystalline hydrocarbon, belonging to one of the unsaturated series. The latter body sometimes occurs to so great an extent that the oil solidifies on cooling. It also contains methyl-nonyl-ketone.

N. O. Zygophylleæ.

Guaiacum Wood Oil.—This oil is identical with that offered in commerce under the name of champaca wood oil. As a matter of fact neither name can be regarded as correct. The wood is known as *Palo balsamo* or guaiacum wood. It was originally believed to be the product of *Guaiacum officinale*, but it is now clearly settled that it is the product of *Bulnesia sarmienti*, and is known as *Palo santo* (holy wood) to the natives. It appears to be indigenous to Argentine and Paraguay, and is especially plentiful along the course of the river Rio Bermejo, a tributary of the Rio Paraguay. The wood yields from 4 to 8 per cent. of essential oil, which is practically solid at ordinary temperatures. This oil has an exceedingly delicate tea odour, and is well suited both for soap perfumery and for blending with stronger perfumes for ordinary scents. The oil, which is of a hard semi-solid consistency, has a specific gravity of about ·970 at 30°, and is laevo-rotary to the extent of about – 6° to – 8° at its melting point temperature. It liquefies at from + 45° to

+ 55°, but rapidly solidifies on cooling. It is soluble in 70 per cent. alcohol. The oil has an ester number of 2 to 4.

The only constituent yet ascertained has been examined by Wallach and Tuttle. It is a crystalline alcohol of the formula $C_{15}H_{26}O$, which is termed guaiol. This body is identical with that found by Merck and named by him champacol, believing that the wood was really champaca wood. Guaiol melts at 91°, boils at 288° under ordinary pressure, and at 155° until a pressure of 13 mm., and is laevo-rotary. By heating it with zinc chloride, it yields a blue oil, of specific gravity ·910 at 20°, and which appears to be a sesquiterpene. An acetate of the alcohol has been prepared, which boils at 155° under a pressure of 10 mm. In addition to its legitimate use as a perfume, it is now being somewhat extensively used as an adulterant of otto of roses. It is usually mixed with geranium oil, so as to have the same congealing point as otto of roses, and is then used under the name "essence de la gaïac à la géranium".

N. O. Anacardiaceæ.

Mastic Oil.—The resin from *Pistacia lentiscus*, the mastic tree, an inhabitant of Southern Europe, North Africa and the Levant, which is known as mastic, consists of a mixture of resins and resinoids with about 1 to 2 per cent. of volatile oil. This oil, which has a characteristic, pleasant odour, has a specific gravity of about ·850 to ·870, and an optical rotation of + 20° to + 30°. Its composition is not known, except that it contains one or more terpenes.

Chian Turpentine Oil.—This oil is the product of distillation with water, of Chian turpentine, the resin of *Pistacia terebinthus*, an inhabitant of Syria and the Greek archipelago. The yield is about 15 per cent. of an oil of specific gravity ·860 to ·870, and optical rotation + 10° to + 20°. It resembles turpentine in its composition.

N. O. Leguminosæ.

Copaiba Oil.—This oil is obtained from several species of *Copaifera.* It is obtained by distilling the oleo-resin commonly known as balsam of copaiba, which yields from 35 to 65 per cent. of essential oil. The principal varieties met with in commerce are the following: Bahia, Cartagena, Maracaibo, Maranham, Para, Cayenne and Angostura. The following are probably the sources of several of these (Umney):—

Bahia, *C. coriacea.*
Cartagena, *C. officinalis.*
Maracaibo, *C. officinalis.*
Maranham, *C. landsdorffii.*
Para, *C. multijuga.*
Cayenne, *C. guianensis.*

Both the "balsam" and the essential oil are official in the *British Pharmacopœia*; but in the description of the essential oil under "copaiba" the optical rotation is given as − 28° to − 35°. This is an error due to incorrect abstraction of a paper where the optical rotation is given for a 200 mm. tube. Apart from this the figures are incorrect (*vide infra*).

Oil of copaiba is a colourless to pale yellow thick oil occasionally of a faint green tinge, of specific gravity varying between 0·900 and 0·918. The optical rotation is very variable, but the figures − 7° to − 20° will be found to cover most genuine samples. Rarely − 5° to − 35° will be found, and Schimmel & Co. record figures as high as − 78° for a sample of Para oil, and as low as − 2° for an Angostura oil. Whether these were pure oils is not clear, but certainly they must be regarded as abnormal. The acid value of the oil is from 2 to 12, and the ester value from 0 to 10. The oil is soluble in one volume of absolute alcohol, and in six to ten volumes of 95 per cent. alcohol. Its refractive index is 1·500, rarely slightly under this figure, usually rather above it. The oil boils between 245° and 280°.

The only constituents of copaiba oil that are known with

certainty are sesquiterpenes, with traces of a sesquiterpene alcohol. In surinam oil it is said that traces of cadinene are present amongst the sesquiterpenes. The usual adulterants of the "balsam" which find their way into the essential oil, are gurjun oil and African copaiba.

Gurjun oil is strongly laevo-rotary, whilst African copaiba oil is dextro-rotary. Mixtures of the two are often found so that the optical rotation is carefully adjusted. But gurjun oil yields a very characteristic reaction which enables it to be detected with almost certainty. If six drops of the oil are dissolved in 15 c.c. of glacial acetic acid and six drops of nitric acid added and the whole shaken, a purple to violet colour will be developed in a minute or two, according to the amount of adulterant present. If after ten minutes no colour or only the very faintest trace of pink is developed no notice need be taken of it, as it will probably be due to traces of a sesquiterpene yielding a faint colour reaction, which occurs in some copaibas. In the absence of gurjun oil, African copaiba oil will lower the rotation or even make it change its sign.

N. O. Burseraceæ.

Linaloe Oil.—The linaloe oil of ordinary commerce is distilled both in Mexico and Europe from the wood of several species of *Bursera*, chiefly from *Bursera Delpechiana* and *Bursera aloexylon*, and is in no way connected with aloe wood, as its name implies (*lignaloe*). A linaloe wood is also exported from French Guiana and Brazil, but this, known locally as *bois de rose femelle* or *licari* wood, is the product of one of the *Lauraceæ*, probably *Ocotea caudata*, and is mentioned here, out of its proper place, as a matter of convenience.

The Mexican wood contains from 7 to 12 per cent. of volatile oil, distributed through the circular strata of woody parenchyma and prosenchyma. It was first investigated by

Verneuil and Poisson, who stated that it distilled almost entirely between 189° and 192°, and that it consisted mainly of an oxygenated body of the formula $2(C_{10}H_8)5H_2O$. Semmler, however (*Berichte*, 1891, p. 207), was the first to discover the true odorous principle of the oil, which he termed linalol. In addition to this alcohol, geraniol and d-terpineol and the ketone, methyl-heptenone, have been found in the oil, together with traces of a sesquiterpene and two terpenes. Barbier and Bouveault give as the composition of an oil examined by them—

Linalol	90 per cent.[1]
Geraniol	2 „
Sesquiterpene	3 „
Methyl-heptenone	0·1 „
Terpene (1)	0·1 „
„ (2)	0·1 „

Theulier has shown that geraniol, terpineol and methyl-heptenone are absent from the Cayenne oil. The oil is of pleasant odour, referred by some to that of lemon and bergamot, but in the author's opinion not in the least similar to either. It varies in specific gravity from ·875 to ·898, and in optical rotation is usually from − 5° to − 12°. It should be quite soluble in two volumes of 70 per cent. alcohol.

It has now been established, however, that linaloe oil is sometimes dextro-rotary up to + 8°. The acid value of the oil is from 1 to 2, and the ester value from 3 up to 20. The refractive index varies between 1·4590 and 1·4640. The determination of the amount of linalol is not an easy matter as this alcohol readily breaks down on heating with acetic anhydride (*vide* p. 117). The results of fractional distillation are most useful, and genuine oils should agree with the following figures which were obtained by the author and Bennett:—

[1] This figure is undoubtedly too high.

No. 1.

		Sp. Gr.	Optical Rotation.	Refractive Index.
1	10%	0·868	−11°	1·4580
2	20%	0·870	−11° 30′	1·4590
3	20%	0·871	−13°	1·4605
4	20%	0·872	−13°	1·4612
5	20%	0·876	−12°	1·4620
6	10% (residue)	0·913	—	1·4750

		No. 2.		No. 3.		No. 4.	
		Sp. Gr.	Optical Rotation.	Sp. Gr.	Optical Rotation.	Sp. Gr.	Optical Rotation.
1	10%	0·870	−10° 30′	0·872	−11° 40′	0·871	−12°
2	20%	0·870	−10° 20′	0·871	−11° 30′	0·871	−13°
3	20%	0·871	−10° 40′	0·873	−12°	0·873	−13° 20′
4	20%	0·873	−10° 10′	0·874	−11° 50′	0·874	−11° 50′
5	20%	0·877	− 9° 40′	0·876	−11° 10′	0·876	−10° 30′
6	(residue)	0·909	—	0·914	—	0·912	—

The characters of the original oils were as follows:—

No.	Sp. Gr.	Optical Rotation.
1	0·882	−11°
2	0·882	−10°
3	0·877	−11° 30′
4	0·879	−12° 10′

Schimmel gives the following figures for two dextro-rotary oils:—

Oil I.: $d_{15°}$ 0·8816; α_d + 6° 3′; acid number 1·7; ester number 20·0; $n_{d20°}$ 1·46209; soluble in 1·6 and more volumes 70 per cent. alcohol. On distillation *in vacuo* there passed over:—

	Pressure.	Temperature.	Per cent.	Optical Rotation.	Remarks.
1	4 mm.	up to 66°	8·5	α_d + 6° 30′	
2	4 ,,	66° to 67·5°	23·5	α_d + 8° 18′	linalol fraction
3	4 ,,	67·5° to 68°	32·1	α_d + 9°	linalol fraction
4	5 ,,	73° to 76°	17·0	α_d + 7° 30′	linalol fraction
5	5 ,,	76° to 82°	2·1	α_d + 3° 20′	
6	5 ,,	82° to 96°	8·7	α_d −10° 5′	

Oil II.: $d_{15°}$ 0·8783; α_d + 8°; acid number 1·4; ester number 3·5; $n_{\alpha 20°}$ 1·46149; soluble in 2·0 and more volumes 70 per cent. alcohol. On distillation *in vacuo* the following passed over:—

	Pressure.	Temperature.	Per cent.	Optical Rotation.	Remarks.
1	10 mm.	60° to 86°	4·5	α_d + 5° 24′	
2	10 ,,	86° to 90°	9·0	α_d + 8° 50′	linalol fraction
3	10 ,,	90° to 91°	15·0	α_d +11° 21′	linalol fraction
4	14 ,,	95° to 97°	51·0	α_d +11° 15′	linalol fraction
5	14 ,,	97° to 100°	5·0	α_d + 8°	
6	14 ,,	100° to 110°	3·0	α_d −11°	
7	14 ,,	110° to 120°	3·0	α_d −18° 20′	

The Cayenne wood has been described under various names, but the researches of Professor Möller have proved that it is the product of one of the *Lauraceæ*, as above mentioned (*Pharm. Post*, 1896, No. 46). The two plants which probably yield the wood are *Ocotea caudata* and *Licaria guaiaensis*. The oil is obtained to the extent of from 1 to 2 per cent., and is of agreeable odour, and specific gravity ·870 to ·880. It is laevo-rotary − 15° to − 17°, and contains the same principal constituents as the oil from the Mexican wood. Linalol, geraniol and methyl-heptenone have been identified. The oil from the Cayenne wood, however, is not much seen in commerce.

Theulier gives the following figures for the Cayenne oil:—

Specific gravity	0·873 to 0·875
Optical rotation	−15° 50′
It is soluble in 2 volumes of 70 % alcohol.	
Ester value	1·4
Boils between	192° to 210°

The following table shows the behaviour of the oil on fractionation :—

Temperature.	*Per cent. distilled.*	*Sp. Gravity.*	*Rotation.*
100°	0·50	—	—
194° to 195°	38·00	0·8625	−15° 48′
195° to 196°	39·00	0·8638	−16° 20′
196° to 200°	16·00	0·8660	−14° 32′
200° to 205°	4·00	—	−11° 50′
Residue	2·50	—	—

Elemi Oil.—Elemi resin yields from 15 to 30 per cent. of volatile oil. The botanical source of the plant yielding the resin is not definitely decided, but it is probably *Canarium commune* and other species. Several kinds of elemi, probably of quite different botanical origin, were offered in commerce at one time, but now practically the whole of the resin on the market is the Manila elemi, which in all probability is the product of *Canarium* species. Flückiger and Hanbury state that the oil is colourless, and strongly dextro-rotary, whilst Deville states that the oil is laevo-rotary. This difference is doubtless due to the resin having been obtained from different plants. Schimmel & Co. distilled some oil and found it to have a specific gravity ·900 and to be dextro-rotary. The oil consists chiefly of the terpenes *dextro*-phellandrene and dipentene, but contains also some higher boiling compounds. It has a specific gravity ·870 to ·910, and is dextro-rotary about + 45° (if distilled from Manila elemi). The oil is but seldom employed.

Myrrh Oil.—The resin obtained from *Commiphora myrrha*, and other species, yields from 2 to 10 per cent. of a volatile oil of specific gravity ·985 to 1·046 and of laevo-rotary power up to − 90°. The chemistry of the

oil requires investigation. Its refractive index is about 1·5360. Its acid value is from 5 to 10, and ester value about 48.

Tucholka (*Arch. Pharm.*, ccxxxv., 289) has extracted the essential oil from a Bisabol myrrh coming from the interior of the Somali country, by removing it from the alcoholic solution of the resin by means of petroleum ether. The oil was purified by steam distillation, and then had a light yellow colour, specific gravity ·8836, and optical rotation − 14° 20′. It boiled at 220° to 270°. The yield was 7·8 per cent. By means of dry hydrochloric acid gas, a crystalline hydrochloride was separated, which, on treatment with boiling acetic solution of sodium acetate, set free a hydrocarbon which the above-named investigator terms bisabolene. This hydrocarbon had a specific gravity ·8914 and boiled at 260°. The same chemist suggests the unlikely formula $C_{56}H_{90}O$ for the residual portion of the oil.

Frankincense Oil.—The oil from the resin of various species of *Boswellia*, which is yielded to the extent of 3 to 8 per cent., has a specific gravity ·875 to ·885 and an optical rotation of about + 20°. Its acid value is about 2 and ester value 15 to 20. It consists chiefly of terpenes, of which those identified are pinene, phellandrene and dipentene. It is also said by Haensel to contain an alcohol of the formula $C_{26}H_{44}O$, and its formic acid ester.

Opoponax Oil.—The resin of *Balsamodendron Kafal* yields from 5 to 10 per cent. of an oil of specific gravity ·860 to ·910 and of optical activity − 8° to − 15°. It contains terpenes, but its chemistry requires investigation. A crystalline body, $C_{20}H_{10}O_7$, melting at 134° and termed oponal, has been isolated. Schimmel & Co. have found an alcohol, and a sesquiterpene of specific gravity 0·871 and refractive index 1·4887, and optically inactive.

N. O. GERANIACEÆ.

Geranium Oil.—True geranium oil is distilled from the fresh herb of several species of pelargonium, chiefly *Pelargonium odoratissimum*, *Pelargonium capitatum* and *Pelargonium roseum*. As a matter of fact, however, the plants cultivated are varieties of these descriptions, not corresponding exactly with the plant when cultivated true to name in England. The plants are cultivated in open fields in many parts of Algeria, notably at La Trappe de Staoüeli, Castiglione, Sahel, and near Algiers and Constantine. It is also largely cultivated in the south of France, in Spain (chiefly near Valencia and in the province of Almeria), in Italy, Corsica, Réunion (Bourbon) and in Provence.

The plants are gathered a short time before the opening of the flowers, when the rose-like odour commences to develop—the leaves at the same time commencing to turn yellow. The odorous oil is contained entirely in the green parts of the plant, the coloured petals being practically odourless. The whole plant is, however, put into the still, and sometimes rose petals are added, and the resulting fine oil is sold as oil of rose-geranium. There has been much controversy between various chemists regarding the identity and nomenclature of the alcohol contained in geranium oils. It is not proposed to enter into these controversies here, as an impartial examination of the subject easily enables one to discriminate the facts of the case, but for a succinct account of them, the reader is referred to Schimmel & Co.'s report for April, 1896.

Geranium oil is a sweet-scented liquid of specific gravity ·888 to ·906. It is laevo-rotary, from – 6° to – 16°. (This oil must not be confused with the so-called Indian geranium oil, the product of one of the Gramineæ, *quod vide.*) Pure geranium oil is soluble in three times its volume of 70 per cent. alcohol. The main constituent of the oil is geraniol,

but some citronellol is also present. In addition to the free alcohols, the tiglic acid esters are also present, together with small quantities of caproic acid esters. Flatau and Labbé state that two other acids, $C_{14}H_{28}O_2$ and $C_{10}H_{18}O_2$, are also present in the form of esters, but this requires confirmation, and is disputed by Schimmel & Co. Acetic, butyric and valerianic oils are also present in traces. The amount of geraniol (together with the citronellol, calculated as geraniol) present is usually about 60 per cent. in the free state, but sometimes reaches 70 per cent. In addition there is from 15 to 25 per cent. combined in the form of esters. Laevomenthone and a stearoptene melting at 63° are present in traces. Schimmel & Co. have recently found linalol, one of the amyl alcohols, pinene and phellandrene present. The refractive indices of a number of geranium oils have been determined, and as the true geranium oil is often adulterated with the so-called Indian geranium oil (*vide Gramineæ*), this figure will be found of use in cases where gross adulteration has been practised. The average figures are as follows :—

African oil	1·4680
Bourbon	1·4640
Spanish	1·4610
French and German	1·4650
Indian oil	1·4800 to 1·4900

The following table covers numerous samples of geranium oils :—

	Specific Gravity.	Rotation.	Esters.[1]	Total Geraniol.
			Per cent.	Per cent.
Réunion oil	·888 to ·896	− 8 to − 11	26 to 33	75 to 85
Cames „	·896 to ·905	− 9°	25 to 28	80
African „	·892 to ·900	− 7° to − 10°	20 to 30	82·1
Spanish „	·898	− 10°	30 to 40	85·5
German „	·906	− 16°	27·9	74·1

[1] Calculated as geranyl tiglate.

Schimmel & Co. give the following limits for the various oils :—

	Sp. Gravity.	*Rotation.*
Algerian	·892 to ·900	− 6° 30′ to − 10°
German	·906	− 16°
French	·897 to ·905	− 7° 30′ to − 9° 30′
Réunion	·889 to ·898	− 8° to − 11°

and state that the Algerian variety is poorest in esters, containing from 19 to 29 per cent. calculated as geranyl tiglate, as against 25 to 35 per cent. for other varieties. Jeancard has found 19 per cent. of esters in a French oil, but this was probably adulterated.

Charabot and Laloue (*Bull. Soc. Chim. de Paris*, 1903, 838) have published an important contribution to that portion of the chemistry of essential oils which Dr. Charabot has so especially made his own. To study the evolution of the various organic bodies found in the essential oils, a study which may eventually lead to the possibility of favourably modifying the odour of oils by artificial means, it is necessary to have an accurate conception of the actual distribution of these bodies. The paper in question deals with the distribution of the organic constituents in the geranium.

In determining the free volatile acids present, they find that the amount diminishes as one proceeds from the leaves down to the stem, the leaves themselves containing 50 per cent. more than the stems. A careful examination of the different portions of the flowering plant, shows that the terpenic compounds (by which the authors evidently mean the geraniol compounds as well) are found to be entirely absent in the petioles and in the stems, being found only in the leaves. It is therefore clear that the odorous substances are elaborated in the leaves themselves. This at once explains the unusual circumstance of the complete absence of essential oil in the flower; for the oil does not at any time traverse the stems, and therefore has no opportunity of reaching the flowers.

The essential oil obtained by separation from the distilla-

tion waters was examined in comparison with that extracted from the water itself, and with the whole of the oil yielded by the plant. The following results were obtained:—

	Separated Oil.	*Oil from Water.*	*Total Oil.*
Specific gravity	0·8979	0·8930	0·8971
Rotation	−11° 2′	−5° 13′	−10° 6′
Acidity	47	16·5	24
Saponification No.	63·6	23·2	57
Ester No.	16·6	6·7	15
Alcohols as geraniol	70·7 per cent.	77·5 per cent.	71·8 per cent.
Esters (*geranyl tiglate*)	7·0 „	2·8 „	6·3 „

A geranium oil produced in Sicily has been examined by Umney and Bennett. This product, which had a pleasant odour, was obtained in a yield of 0·07 per cent. from plants grown on a dry soil. The optical rotation of the 80 per cent. first distilling over was − 11°; $d_{15°}$ 0·894; ester content (geranyl tiglinate) 35·6 per cent.; total geraniol 71·9 per cent.; soluble in two vol. 80 per cent. alcohol; insoluble in 70 per cent. alcohol. The ester content is therefore higher than in French or Algerian oils, but approaches very closely to the highest observed in Réunion geranium oil. In view of the small yield in which it was obtained in the distillation, it is doubtful whether the Sicilian oil will ever appear as a serious competitor against the oils met with in commerce.

Schimmel & Co. have found interesting adulterations of geranium oil. From two samples they isolated benzoic acid which had probably been added to the oil in the form of ester, in order to cause an apparent increase in the content of geranyl tiglinate in the oil. The oils gave the following results on examination:—

1. $d_{15°}$ 0·9074; a_d − 9°; $n_{d20°}$ 1·47196; acid number 6·6; ester number 74·8 = 31·5 per cent. geranyl tiglate; ester number after acetylation 222·64 = 73·5 per cent. total geraniol; soluble in 1·8 and more volumes 70 per cent. alcohol; the dilute solution is opalescent; when left standing, a fairly large

separation of paraffin occurs. The benzoic acid isolated melted at 121° to 122°.

2. $d_{15°}$ 0·9054; a_d - 8° 8′; $n_{d20°}$ 1·47313; acid number 6·9; ester number 61·3 = 25·8 per cent. geranyl tiglate; soluble in about two and more volumes 70 per cent. alcohol.

Fatty oils and turpentine are frequently added to the pure geranium oil, but these are easily detected by the decrease in the solubility of the oil, besides the alteration in the other constants. Fatty oils also leave a residue on evaporation. Indian geranium oil lowers the ester value, and raises the refractive index, and raises the free geraniol content. Geranium oil is extensively used as a perfume on account of its exquisite odour, and other leaves are sometimes added to the geranium leaves on distillation, in order to produce a still finer product, *e.g.*, rose geranium oil. The geranium oil used so extensively for adulterating otto of roses is not the true geranium oil, but that usually known as Turkish or Indian geranium (*vide supra*).

N. O. Tropæoleæ.

Oil of Tropæolum.—The Nasturtium (*Tropæolum majus*) yields about ·04 per cent. of a strongly smelling essential oil, when the green plant is distilled with steam. The vessel should be well tinned inside, on account of the sulphur contained in the oil. Hofmann investigated this oil in 1874, probably distilling it without previous crushing. In the oil he found benzyl cyanide. Gadamer (*Arch. Pharm.*, 1899, p. 237) distilled the plant, first well minced, with steam, and extracted the small quantity of oil from the distillate with ether. He found that it contained 86 per cent. of benzylthiocarbimide. He considers this is due to the fact that there is in the plant an enzyme which decomposes the glucoside present, with the formation of this body. He suggests that by not crushing the plant the enzyme is destroyed before

it can decompose the glucoside which is distributed all through the cells, and that the benzyl cyanide obtained by Hofmann was a product of decomposition of the glucoside through the distillation.

N. O. Meliaceæ.

Oil of Cedrela.—One of the most useful woods in Jamaica is that obtained from *Cedrela odorata*, an immense forest tree. It is a native of the Caribbee Islands and the Barbadoes. Its timber has a pleasant odour of cedar, hence it is frequently spoken of as Jamaica or Honduras cedar, and from the wood most of the ordinary cigar boxes are made. The wood yields from ·5 to 1 per cent. of oil of a light blue colour, of specific gravity ·935, and optical rotation under − 1°. The cedar-wood oils from La Plata and Punta Arenas (Costa Rica), which have been referred to under true cedar-wood oil, are probably obtained from closely related trees of this order. The oil from La Plata is of a light blue colour, has a specific gravity ·928, and is optically inactive. That from Punta Arenas is yellow, of specific gravity ·915 and optical rotation − 6°. It consists chiefly of cadinene.

Corinto cedrela wood yields an oil of specific gravity 0·906 and optical activity − 17°. A Cuban wood gave an oil of specific gravity 0·923 and optical activity +18°, consisting largely of cadinene.

N. O. Cruciferæ.

Mustard Oil.—The essential oil of mustard is obtained by distilling the seeds of *Sinapis nigra* with water. The oil is official in the *British Pharmacopœia*, which requires it to have a specific gravity of 1·018 to 1·030. The seeds contain the glucoside potassium myronate, which, under the influence of a ferment, myrosin, also present in the seeds, in the presence of water, is decomposed according to the following equation :—

$$\underset{\text{Potassium myronate.}}{C_{10}H_{18}KNO_{10}S_2} = \underset{\text{Glucose.}}{C_6H_{12}O_6} + SO_4KH + \underset{\text{Mustard oil.}}{CS.N.C_3H_5}.$$

The chief product of the reaction is thus allyl iso-thiocyanate (allyl thiocarbimide), a pungent and disagreeable liquid. A small quantity of the normal allyl thiocyanate is also formed, together with traces of allyl cyanide and carbon disulphide. The oil is a pungent and unpleasantly smelling liquid of specific gravity 1·015 to 1·030, and optically inactive. It boils almost entirely from 148° to 156°. Its refractive index is 1·526 to 1·530. As mustard oil consists almost entirely of allyl iso-thiocyanate, and the latter body is easily prepared artificially, there is an artificial oil on the market. This is made by distilling allyl iodide or bromide with alcoholic solution of potassium thiocyanate — a molecular rearrangement to the iso-thiocyanic radicle taking place. Thus—

$$CN . SK + C_3H_5I = CS . N . C_3H_5 + KI.$$

Pure allyl iso-thiocyanate is a liquid of specific gravity 1·017 at 10°, boiling at 151°.

The artificial oil, however, is not far different in price from the natural oil. The amount of allyl iso-thiocyanate present in the oil can be approximately estimated by heating a known quantity with an alcoholic solution of ammonia, when allyl-thio-urea is formed. There are several methods of determining the amount of thiocyanate present. Three grammes of the oil and 3 grammes of alcohol are shaken in a flask with 6 grammes of a 10 per cent. solution of ammonia. It should become clear after standing for a few hours, or rapidly if warmed to 50° C., and deposit crystals of allyl-thio-urea (thiosinamine)

$$CS\begin{matrix}NH . C_3H_5\\ NH_2\end{matrix}$$

To determine the quantity, decant the mother liquor and evaporate it slowly on the water bath in a tared capsule, adding fresh portions slowly as the smell of ammonia disappears. Then add the crystals from the flask to those in

the capsule, rinsing the flask with a little alcohol, and heat the capsule on the water bath to a constant weight. Three grammes of oil should yield between 3·25 and 3·5 grammes of thiosinamine, which should melt at 70° to 74°. 116 parts of thiosinamine correspond to 99 parts of allyl iso-thiocyanate. Gadamer (*Arch. Pharm.*, 1899, pp. 110, 237) recommends the following process. The mustard oil is dissolved in alcohol to form an exactly 2 per cent. solution. Five c.c. (4·2 grammes) of this solution are allowed to remain with 25 c.c. of decinormal solution of silver nitrate and 5 c.c. of ammonia for 24 hours in a well-stoppered 50 c.c. flask. It is then made up to 50 c.c. with water and filtered from the precipitated silver sulphide; 25 c.c. of the filtrate are mixed with 4 c.c. of nitric acid and a few drops of ferric sulphate solution, and titrated with decinormal ammonium thiocyanate solution, until the characteristic red colour of the ferric thiocyanate appears. From 4·1 to 4·5 c.c. of the solution (corresponding to 1·85 to 2·0 per cent. of allyl thiocyanate in the alcoholic solution) should be required.

Grützner converts the thiocyanate into thiosinamine, which he oxidises with hyperoxide of sodium, and weighs the resultant sulphuric acid as barium-sulphate. From the figures obtained in his analyses, Grützner concludes that a mustard oil containing 28·60 per cent. of sulphur (equivalent to 88·48 per cent. of iso-thiocyanate) may be regarded as pure. P. Roeser proposes to modify Gadamer's method for the determination of the sulphur content of oil of mustard so as to determine the excess of silver nitrate in an ammoniacal solution, instead of an acid solution according to Volhard's method, as is usually done. According to this, the process should be as follows. When the conversion of the thiosinamine with silver nitrate, after 24 hours' standing, has taken place, an excess of one-tenth normal solution of potassium cyanide is added to 50 c.c. of the clear filtrate, and the excess of potassium

cyanide titrated back with one-tenth normal solution of silver nitrate, in the presence of a few drops of a weak ammoniacal solution (5 per cent.) of potassium iodide.

Schimmel & Co. prefer the following method. About 5 grammes of a solution of 1 gramme mustard oil in 49 grammes alcohol are mixed in a measuring flask of 100 c.c. capacity with 50 c.c. decinormal solution of silver nitrate and 10 c.c. ammonia liquid ($d_{15°}$ 0·960); the flask is then closed, and with frequent agitation left standing for 24 hours with the light excluded. The flask is then placed for half an hour in water at 80°, during which time it is again repeatedly shaken, then cooled down to the temperature of the room, filled up with water to the mark, shaken up, and filtered. Fifty c.c. of the filtrate are titrated with one-tenth normal solution of ammonium sulphocyanide, after adding 6 c.c. nitric acid ($d_{15°}$ 1·153) and a small quantity of solution of iron alum, until a change of colour from white to red takes place. In order to ascertain the whole quantity of silver solution which has entered into reaction, the number of c.c. of ammonium sulphocyanide solution used up is doubled, and the product subtracted from 50. The percentage of allyl isothiocyanate in the mustard oil is obtained by means of the following formula:—

$$\%\ CSNC_3H_5 = \frac{a\ 24{\cdot}7875}{b}$$

a = number of c.c. of decinormal solution of silver nitrate used up, b = spirit of mustard used, in grammes. Mustard oil determinations carried out by them in the manner described, showed in the case of natural oil a content of about 94 per cent. allyl isothiocyanate, whilst in artificial oil about 98 per cent. was determined.

White mustard seeds, from *Sinapis alba*, contain the glucoside sinalbin, $C_{30}H_{44}N_2S_2O_{16}$, which on decomposition in the same manner as the glucoside of black mustard yields glucose, sinapine sulphate, and the evil-smelling oil, acrimyl-

thiocarbimide (*p*-hydroxy-benzyl-iso-thiocyanate). The reaction takes place as follows:—

$C_{20}H_{24}N_2S_2O_{16} = C_6H_{12}O_6 + C_{16}H_{23}NO_5 \cdot H_2SO_4 + C_7H_7O \cdot NCS.$

Acrimyl iso-thiocyanate, or "white mustard oil," is a yellowish oily liquid, of pungent odour and unpleasant hot taste. It is prepared synthetically by treating *p*-hydroxy-benzylamine with carbon disulphide, and the resulting compound with mercuric chloride.

Cochlearia Oil.—Cochlearia or spoonwort oil is distilled from the fresh-flowering plant *Cochlearia officinalis* (scurvy grass), which yields a very small quantity of the essential oil. The specific gravity of the oil is about ·930 to ·950, and it is dextro-rotary to the extent of + 50° or thereabouts. Hofmann showed many years ago that the principal constituent was secondary butyl-iso-thiocyanate, of the formula—

$$CS \cdot NCH\begin{matrix}C_2H_5\\CH_3\end{matrix}$$

Gadamer (*Arch. Pharm.*, 1899, p. 237) has shown that if the dried plant without flowers is cut up, and some white mustard flower is added, the yield of oil is much increased. From 28 kilos of the dried plant, which is known as scurvy grass, 66 grammes of essential oil were obtained. The oil boiled at 150° to 162°, and the bulk of the oil was found to be secondary butyl-iso-thiocyanate. The amount of iso-thiocyanate was estimated by dissolving a weighed quantity of the oil in alcohol, adding excess of decinormal solution of silver nitrate, allowing the whole to remain for 24 hours in a well-stoppered bottle, filtering from the precipitated silver sulphide, and titrating the excess of silver with ammonium thiocyanate solution. The fractions of the oil of higher boiling point (156° to 162°) had a lower specific gravity and higher optical rotation than the earlier fractions. They possibly contained a little limonene.

In order to determine the purity of the oil a quantity may

be heated on the water bath with 10 per cent. of its weight of ammonia for a few hours under a condenser, and the liquid evaporated to dryness. The mass is then extracted with alcohol and the liquid filtered and evaporated on a watch glass; the resulting crystals of crude secondary butyl-thio-urea melt at 125° to 135°. Pure secondary butyl-thio-urea melts at 136° to 137°. An artificial cochlearia oil exists, but appears to consist of iso-butyl-iso-thiocyanate. The crystalline thiocarbimide yielded by this melts at 93·5°. The usual adulterants can be thus detected, as the thiocarbimides (thio-ureas) formed from them melt at the following temperatures :—

Allyl (mustard oil)	72° to 74°
Normal butyl	79°
Iso-butyl	93·5°
Tertiary butyl	165°

Horseradish Oil.—The oil of *Cochlearia Armoracia*, which is yielded in very small quantity, contains allyl iso-thiocyanate (mustard oil). Its specific gravity is 1·010.

N. O. Cistineæ.

Ladanum Oil.— Messrs. Schimmel & Co. distilled a parcel of old ladanum resin, the product of *Cistus creticus*, and obtained therefrom ·9 per cent. of essential oil. *Cistus creticus* is the Cretan rock rose, a native of rocky ground in Macedonia, Thrace, Greece and the islands of Crete, Rhodes, Sicily and Cyprus. Its botanical relationships are hardly decided, as it is regarded by some as being merely a variety of *Cistus villosus* (Linn.). In Cyprus the ladanum (*labdanum*) is chiefly collected by the shepherds from the fleeces of the sheep, who unconsciously collect it from the plants whilst pasturing, the leaves becoming very viscid with the secretion. The oil obtained by Schimmel & Co. had a specific gravity 1·011 and had a fine ambergris odour; after keeping for a few months, crystals to the extent of 25 per cent. were deposited, which have not been thoroughly examined. This oil appears

to have been known in the sixteenth century, as a reference is made to it in the *Gross Destillirbuch* by Ryff, published in 1542. An oil has also been distilled from the leaves of *Cistus ladaniferus*, an allied plant, probably a native of Portugal, but very common in Spain. It has a specific gravity ·925.

N. O. Magnoliaceæ.

Champaca Oil.—The so-called champaca wood oil, commonly known as guaiacum wood oil, must not be confused with the true champaca oil. The first-named is the product of an entirely different plant. The true champaca oil is distilled from the flowers of *Michelia Champaca*, a plant cultivated, and also growing wild, in the forests of the Himalayas, from Nipal and Kumaon eastwards; and also in the Nilghiris and Travancore, Java and the Philippines. The flowers, which are of an exquisite odour, are not unlike a double narcissus. The essential oil distilled from the flowers is known in India as *Pand* or *Champa-ka-utter*. The oil is known as *Yellow Champaca*, whilst that from *Michelia longifolia* is known as *White Champaca*. Both oils contain benzoic acid. A sample of the former distilled in Java (yellow champaca oil) was a pale yellow oil of thin consistency, resembling, in a degree, oil of orris in odour. It had a specific gravity ·914, and an optical rotation – 13° 14′. An oil of white champaca from the same source was found to have a specific gravity ·883 and an optical rotation – 12° 50′. Its odour recalled that of basil. According to older statements by Schimmel & Co., the specific gravity of the oil from *Michelia champaca* varies from ·907 to ·940 and the optical rotation from – 12° 18′ to – 55°. The saponification value is about 77°.

The properties of the oil according to their more recent statements are $d_{15°}$ 0·8861; a^d – 11° 10′; acid number, 10·0;

ester number, 21·6; ester number after acetylation, 150·1; soluble in 2 vol. 70 per cent. alcohol; when 4 vol. and more are added, strong turbidity; soluble in 1 vol. and more 80 per cent. alcohol, when more than 7 vol. are added, opalescence (separation of paraffin). The oil has a bright brown colour and shows, especially in alcoholic solution, a very feeble bluish fluorescence, which may possibly be due to the presence of anthranilic acid ester. Of alcohols, linalol appears to be present in the oil, but owing to the small quantities of oil at their disposal, they were unable to obtain an exact proof of this.

Winter's Bark Oil.—The bark of *Drimys Winteri* yields between ·5 and 1 per cent. of this oil. This plant was originally discovered by Captain Winter in the Straits of Magellan, and is now found in various countries from Mexico to Cape Horn. The oil, which has been examined by Avata and Canzoneri, has a specific gravity of about ·945. It consists of a mixture of several bodies from which these chemists state that they have isolated a sesquiterpene. It distilled between 260° and 265° and had a specific gravity ·9344 and a rotary power $[\alpha]_d = +11° 2'$. They term this body winterene, but its chemical identity cannot be regarded as settled.

Para-coto bark yields 1·5 per cent. of essential oil. By some this bark has been credited to *Drimys Winteri*, but its botanical origin is not definitely known. According to Wallach and Reindroff, the oil contains the sesquiterpene cadinene, and also methyl eugenol. It has a specific gravity of about 1·02 and a rotation of + 5° 40′. It is completely soluble in 5 volumes of 70 per cent. alcohol.

N. O. Resedaceæ.

Mignonette Oil.—The fresh flowers of the mignonette, *Reseda odorata*, yield traces, about ·002 per cent., of an

essential oil of exceedingly powerful odour. This oil is semi-solid at ordinary temperatures, and its chemistry is not understood, as the oil is in itself so very rare. Indeed, commercially, an ordinary floral extract is generally used in preference to any direct preparation of the oil. The fresh roots of this plant yield from ·01 to ·04 per cent. of an unpleasantly smelling oil recalling the odour of radishes. This oil contains phenyl-ethyl-thiocarbimide, $C_2H_4(C_6H_5)NSC$, and is a liquid of specific gravity 1·01 to 1·09 and optical rotation about + 1° to + 2°.

N. O. Turneraceæ.

Damiana Oil.—The leaves of various species of *Turnera* (chiefly *Turnera diffusa* and *Turnera aphrodisiaca*) yield about 1 per cent. of oil on distillation. This has a specific gravity ·940 to ·990, and an optical rotation of − 23° to − 25°. It contains a considerable amount of esters, requiring between 4 and 5 per cent. of KOH to saponify it, and deposits, when cooled, a crystalline body, which is probably a paraffin hydrocarbon. The oil finds no employment.

N. O. Clusiaceæ.

Canella-bark Oil.—The bark of *Canella alba* yields from ¾ to 1 per cent. of essential oil. In the drug trade this bark is known frequently as "wild cinnamon," and is found in the south of Florida, the Bahamas, Cuba, Jamaica, Martinique, Barbadoes, etc. The whole tree is very aromatic, especially the flowers, which perfume the neighbourhood for a considerable distance, although they seldom open. The bark is brought to Europe in the form of long quills, rather thicker than those of cinnamon. The taste of the bark somewhat resembles a mixture of cloves and cinnamon, being hot, bitter and aromatic. Meyer and Reiche investigated the oil, of which they obtained ·94 per cent. from the bark, so long ago as 1843, and stated that they isolated four

distinct bodies from it. The first was eugenol, the second was described as being closely allied to the principal constituent of oil of cajuput, and the other two were not closely investigated. Flückiger and Hanbury obtained ·74 per cent. of oil from the bark, and stated that it consisted of two parts of an oxygenated body mixed with one part of a hydrocarbon resembling a mixture of mint and cajuput oils. Eugenol, however, remained as the only well-defined body yet ascertained as a constituent of the oil, till 1890, when Schimmel & Co. showed that the body referred to by Meyer and Reiche as resembling the principal constituent of cajuput oil was actually identical with this, being the now well-known cineol. Williams (*Pharm. Rundschau*, 1894, p. 183) has later examined the oil, and has identified pinene and caryophyllene in it. The specific gravity of the oil ranges from ·920 to ·935 and the optical rotation from + 1° to + 3°.

N. O. Dipterocarpeæ.

Gurjun Balsam Oil.—The so-called wood oil or gurjun balsam is the product of several species of *Dipterocarpus*. This body is an oleoresin, and is used to some extent for adulterating balsam of copaiba. On distillation with water the oleoresin yields from 40 to 70 per cent. of a volatile oil of specific gravity ·915 to ·930 and optical rotation − 35° to − 106°. It contains a sesquiterpene (cadinene?), but its chemistry is not well understood, and requires investigation. It yields a characteristic colour reaction which aids its detection when added to copaiba oil (*q.v.*).

N. O. Ternstrœmiaceæ.

Tea Oil.—According to Müller, the leaves of the tea plant yield from ·6 to 1 per cent. of essential oil. There seems little doubt but that such a large quantity as this must have been obtained from tea artificially scented, but Dr. Van Romburgh has obtained about ·006 per cent. from genuine

tea, and found that the chief product of distillation of the leaves was methyl alcohol. Schimmel & Co. have examined samples obtained from partly fermented leaves, and suggest that the oil may be the result of the fermentation process. Two oils had the specific gravities ·866 and ·8557, and were only very faintly optically active. The principal constituent was found to be methyl alcohol, with possibly a little acetone (which were recovered from the watery liquid, not forming a portion of the oil proper). In the oil, methyl salicylate and a body of the formula $C_6H_{12}O$, which appeared to be of an alcoholic nature, were detected. At all events, the latter body yielded compounds with acetic and benzoic acids.

N. O. Malvaceæ.

Musk Seed Oil.—The seeds of *Hibiscus abelmoschus* yield from ·1 to ·3 per cent. of essential oil of fine odour, known as oil of ambrette, or musk seed oil, having a specific gravity ·900 to ·905, and an optical rotation of 0° to + 1° 30′. It is semi-solid at ordinary temperatures, and probably contains some palmitic acid. A sample of Java distilled oil, however, was liquid at ordinary temperatures, and a French oil of specific gravity ·908 did not solidify at − 10°. This oil requires investigation. The saponification number is from 180 to 200.

N. O. Ranunculaceæ.

Nigella Oil.—The seeds of *Nigella damascena* yield ·5 per cent. of essential oil of specific gravity ·895 to ·906. This oil is fluorescent, and has an odour resembling strawberries. The fluorescence is due to a basic substance termed damascenine, $C_9H_{11}NO_3$. It melts at 26°. Schimmel & Co. have also distilled an oil from the seeds of *Nigella sativa*, which yielded ·46 per cent. of a non-fluorescent oil, of specific gravity ·875, and rotation + 1° 26′. It distilled between 170° and 260° and

had an unpleasant odour, not at all resembling that from *Nigella damascena*.

N. O. Anonaceæ.

Oil of Cananga.—Oil of Cananga or Ylang-Ylang oil ("flower of flowers") is the product of distillation of the flowers of *Cananga odorata*, a native of Ava and Tenasserim, and generally distributed and cultivated throughout Southern Asia. When wild, the tree grows to its maximum height, but its flowers are said to be almost odourless. The cultivation of the plant reaches its highest degree of perfection in the Philippine Islands, and the best variety of the oil is distilled in Manila, where the industry is carried on in a scientific manner. A large quantity of oil also comes from Java and the neighbourhood, but the oil is not nearly of so fine an odour as that from the East Indies. How far this is due to climatic conditions, and how far to the less scientific methods used in the distillation of the oil, it is difficult to say. There appears to be very little doubt but that the tree is the same in both cases.

Genuine Ylang-Ylang oil has a specific gravity of ·930 to ·950 (East Indian) or ·910 to ·940 (Cananga). The optical rotation is − 38° to − 45° (East Indian), and − 17° to − 55° (Cananga). The oil is soluble in from ½ to 2 volumes of 95 per cent. alcohol, and becomes turbid on further addition of alcohol, but without the deposition of oily globules. On steam distillation, a residue of about 5 per cent. is left, so that anything in excess of this figure will probably be a fatty oil—a common adulterant of Ylang-Ylang oil. The ester value lies between 10 and 40; higher numbers indicate the presence of a fatty oil. The decreased solubility in alcohol will also indicate the presence of this adulterant. The earliest investigation of this oil was that of Gal (*Comptes Rendus*, 1873, 16th June), who showed the presence of benzoic acid in the form of esters.

Convert (*Arch. du Pharm.*, 1881, p. 218) confirmed the presence of benzoic esters, and also detected acetic acid in the form of esters in the oil. He also considered it probable that there was a small quantity of either an aldehyde or ketone present. Reychler (*Bull. Soc. Chim.*, 1894, pp. 407, 583, 1045) has since shown that linalol and possibly geraniol exist, together with the sesquiterpene cadinene. Pinene, *p*-cresol methyl ether, and a crystalline solid melting at 138°, probably a sesquiterpene alcohol, have also been shown to be present. So that the following bodies, in addition to others not yet identified, have been found in the oil. Pinene, linalol, geraniol, benzoic and acetic esters, cadinene, *p*-cresol methyl ether, and the crystalline body above referred to. Eugenol has been found in Cananga oil and iso-eugenol in Ylang-Ylang oil. Probably other compounds have been identified, as a synthetic oil closely resembling the natural oil is on the market, but the discoverers prefer to keep their work unpublished. East Indian oil appears to have more low-boiling constituents and esters, but less sesquiterpene than the Java oil.

This oil finds a very extensive use in fine perfumery and is somewhat expensive—the East Indian product especially. An exact examination of both varieties of the oil is greatly needed.

For a useful summary of the botanical relationships of this plant, the reader is referred to Sawyer's *Odorographia*.

CHAPTER VI.

THE CHEMISTRY OF ARTIFICIAL PERFUMES.

THE present chapter is not intended to deal at large with natural perfumes such as civet, musk, ambergris, etc. This subject is more properly treated in works on materia medica and botany, and the present chapter will be devoted to a purely chemical account of a few well-defined active principles of certain natural perfumes other than essential oils, together with a description of the more important synthetic and artificial perfumes. It is here necessary to draw attention to the fact that by far the larger proportion of artificial perfumes which are quoted in price lists are merely skilful mixtures of a few well-defined bodies. The following bodies comprise the more important well-defined artificial perfumes, some of which have necessarily received mention in Chapter V.[1]

Vanillin.—This body is the active odorous ingredient of the vanilla pod, in which it occurs to the extent of about 2 per cent., appearing on the surface of the bean as a fine white crystalline efflorescence. It occurs naturally also in Sumatra benzoin (about 1 per cent.), Siam benzoin (·15 per cent.), and the balsams of Tolu and Peru (traces). Numerous other bodies have been recorded as containing it, such as: Asafœtida (Schmidt, *Arch. Pharm.* [3], xxiv., p. 534); beetroot and asparagus (Lippmann, *Berichte*, xviii., p. 3335); the seeds of *Lupinus albus* (Campani, *Chem. Centr.*, 1888, p. 377); the

[1] The author is much indebted to Dr. Philippe Chuit, of Messrs. Chuit, Naef & Co., of Geneva, for a liberal supply of synthetic perfumes.

seeds of *Rosa canina* (Schneegans, *Jour. Pharm.*, 1890, p. 97), etc., etc.

It was first artificially prepared by Tiemann from the glucoside coniferin, which occurs in the cambium of various coniferous woods. The constitution of vanillin is that of methyl protocatechuic aldehyde $C_6H_3(COH)^1(OCH_3)^3(OH)^4$, and coniferin $C_{16}H_{22}O_8 + 2H_2O$, which is a glucoside melting at 185°, was the substance which Tiemann first used for preparing vanillin from, and for whose process Haarmann and Reimer took out a patent. Coniferin was decomposed, either by emulsin or by boiling with dilute acids, into glucose and coniferyl alcohol $C_6H_3(OH)(OCH_3)C_3H_4OH$, and this body on oxidation yields vanillin; or the oxidation may take place first and the hydrolysis afterwards. The process then consisted of the following reactions. When coniferin is oxidised with an aqueous solution of chromic acid it is converted into gluco-vanillin $C_6H_3(O.CH_3)(O.C_6H_{11}O_5)(CHO)$, the glucoside of vanillin, a crystalline body melting at 170°. For this purpose a solution of 10 parts of coniferin in 200 parts of water is treated at the ordinary temperature with a solution of 8 parts of chromic acid dissolved in a small quantity of water, and the mixture allowed to stand for several days. Barium carbonate is then added to precipitate the chromium. The solution is evaporated to a small bulk, treated with alcohol and filtered. The filtrate on evaporation yields crystals of gluco-vanillin, melting at 170°. On treating this body with the ferment emulsin, or by boiling it with dilute mineral acids, it is decomposed into glucose and vanillin. The latter may be extracted with ether. This process, however, has only an historical interest to-day.

The most important method, however, by which vanillin is now prepared is by the oxidation of eugenol, the chief constituent of oil of cloves. This process proved the subject-matter of a patent taken out in England in 1876 by Tiemann,

and an almost simultaneous one in France by De Laire. The eugenol was instructed to be separated by diluting the oil with three times its volume of ether and agitating the ethereal solution with a dilute solution of potash or soda. The aqueous liquid is separated and acidified, and the eugenol separated by extraction with ether. The eugenol is first acetylated by means of acetic anhydride, and the resulting acet-eugenol is dissolved in acetic acid and oxidised with permanganate of potassium. The liquid is then filtered, and rendered alkaline, and the whole is then evaporated, and the residue treated with moderately dilute acid, and extracted with ether. The ethereal solution is extracted with a solution of sodium bisulphite, which combines with the vanillin. The double sulphite compound is decomposed with dilute sulphuric acid, and the vanillin is extracted with ether, from which solvent it is obtained in fine white crystals.

The best yield, however, is obtained by first converting the eugenol into iso-eugenol $OH . OCH_3 . C_6H_3 . CH : CH . CH_3$ by treating it with solution of potassium hydrate. The acetylation product is oxidised, by which acetyl-vanillin is chiefly formed, which yields vanillin by splitting off the acetyl group.

Vanillin is also obtained by starting from meta-amido-benzaldehyde, which is converted into its diazo compound, which yields meta-oxy-benzaldehyde on treatment with water. These reactions may be represented as follows:—

$$C_6H_4\begin{cases}NH_2^{(1)}\\COH^{(3)}\end{cases} + NOHO + HNO_3 = C_6H_4\begin{cases}N_2 . NO_3\\COH\end{cases} + 2H_2O$$

Meta-amido-benzaldehyde. *Diazo nitrate.*

$$C_6H_4\begin{cases}N_2 . NO_3\\COH\end{cases} + H_2O = C_6H_4\begin{cases}OH^{(1)}\\COH^{(3)}\end{cases} + N_2 + HNO_3$$

Meta-oxybenzaldehyde.

The *meta*-oxybenzaldehyde is then nitrated and methylated, by which means *para*-nitro*meta*-methoxy-benzaldehyde

$C_6H_3 . NO_2^{(4)} . OCH_3^{(3)} . COH^{(1)}$ is formed. By reduction this is altered to the corresponding amido-aldehyde, which is again diazotised and the amido-group replaced by hydroxyl in the usual way, when *para*-oxy*meta*-methoxy-benzaldehyde results, which is, of course, identical with vanillin, or protocatechuic aldehyde methyl ether, $C_6H_3 . COH^1 . OCH_3^3 . OH^4$. Another complicated method, which is the subject of a patent, is to nitrate *meta*-methoxy-cinnamic acid methyl ester, by which means the corresponding *meta*-methoxy-*para*-nitro-cinnamic methyl ester is formed. This body $C_6H_3.OCH_3^{(3)}.NO_2^{(4)}.(C_2H_2CO_2CH_3)^{(1)}$ is hydrolysed and the free acid is converted into its ammonium salt, which is dissolved in water and reduced to the corresponding *meta*-methoxy-*para*-amido-cinnamic acid. This is diazotised in the usual way, and the amido-group is replaced by hydroxyl, by which means an acid termed ferulic acid is formed. This is *meta*-methoxy-*para*-oxycinnamic acid $C_6H_3(OCH_3)OH . (C_2H_2COOH)$. This acid is oxidised (best as an acetyl compound) with potassium permanganate, and thus converted into vanillin. The two methods last described, *viz.*, those starting from *meta*-oxybenzaldehyde and methoxycinnamic acid are only of theoretical interest.

Vanillin is also produced in several ways from guaiacol. A recent patent (D.R.P. 189, 307—German patent) for this is as follows. Guaiacol is treated with hydrocyanic acid in the presence of hydrochloric acid and zinc chloride. The reaction mass, after forty-eight hours, is treated with hot water and filtered; the unaltered guaiacol is removed by extracting the vanillin from ethereal solution by means of sodium bisulphite and recovering it in the usual manner. Care must be taken to remove all traces of guaiacol, as the slightest taint with this phenol entirely spoils the odour and flavour of the vanillin.

There are other methods of obtaining vanillin synthetically, but for fuller details the reader is referred to the various

patent specifications of the German Patent Office (D.R.P. 63,007, 63,027, 72,600, 37,075, 33,229).

Vanillin forms fine white needles melting at 81° to 82° and possessing an intense vanilla odour. Some of the cheaper commercial samples are heavily adulterated with the quite odourless compound, acetanilide. The effect of this body is to lower the melting point even if present in large quantity, but it is very easily detected, as by boiling with solution of potash, aniline is formed, which is easily detected by any of the usual reactions. A quantitative separation may be effected as follows. The substance is dissolved in ether and the liquid repeatedly shaken with concentrated solution of sodium bisulphite. The vanillin is thus extracted, and the ether, after being washed twice with water, is allowed to evaporate, when the acetanilide remains. This will then be found to have a melting point close to 113°. Benzoic acid and coumarin are also occasional adulterants of vanillin. A little isovanillin $C_6H_3(CHO)^1(OH)^3(OCH_3)^4$ is occasionally present, but this is due to the fact that it is generally formed in small quantity with vanillin, in many reactions. The following figures are of great interest as showing the effect of improved manufacturing processes, advances in chemical discovery, and the opposition of rival patentees. The approximate prices of vanillin per lb. were as follows in the years quoted:—

1876	£160	1888	£16
1877	90	1889	16
1878	56	1890	16
1879	36	1891	15 10s.
1880	36	1892	15 10s.
1881	28	1893	15
1882	23	1894	15
1883	21	1895	13
1884	24	1896	13
1885	17 10s.	1897	2 18s.
1886	16	1898	2 12s.
1887	16	1906	18s.

The following remarks on the use of vanillin are from one of Schimmel & Co.'s reports: "In confectionery and chocolate factories, etc., pure crystalline vanillin can be most advantageously used in the form of a 2½ per cent. vanillin sugar, which weight for weight equals in aroma the best vanilla, and should be used in precisely the same manner. Take of crystallised vanillin 25 gr. (ʒ VI gr. XV), dissolve it in 100 gr. (fl. ʒ IV) of pure, odourless absolute alcohol, pour this solution upon 975 gr. (= 2 lb. 2 oz.) of the finest sugar, and mix it thoroughly in order to distribute it as equally as possible. After having evaporated the alcohol in a warm place, and when the sugar has become thoroughly dry, it should be powdered in an earthenware mortar and sifted. It is then ready for use, and may be kept an indefinite time without losing aroma. The yellow spots which occur on the sugar after drying are caused by the vanillin.

"This 2½ per cent. vanillin sugar should not be confounded with the vanilla sugar generally used by confectioners. In order to prepare the latter it is only necessary to add to pure sugar as much of the 2½ per cent. vanillin sugar as would otherwise have been taken of the finest vanilla.

"For liqueur making crystallised vanillin is best used in the form of a 2½ per cent. vanillin essence which, weight for weight, equals the best vanilla in aroma, and is used exactly like it.

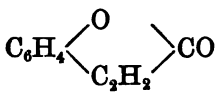
"Take of crystallised vanillin 25 gr. (ʒ VI gr. XV), dissolve it in 490 gr. (fl. ʒ XX) of pure absolute alcohol, and add 485 gr. (fl. ʒ XV) of distilled water.

"The vanilla essence generally used for liqueur making is prepared by taking for that purpose as much of the 2½ per cent. vanilla essence as would otherwise have been taken of the finest vanilla.

"For 100 litres (22 gallons) of liqueur 5 grammes (75 gr.)

of vanillin, or 200 gr. (= fl. ℥ vii) of 2½ per cent. vanillin essence, are usually employed."

Coumarin $C_9H_6O_2$ is, chemically, the δ-lactone of coumarinic acid, of the constitution—



It is a white crystalline solid, melting at 67° and distilling at 290°. It is soluble in hot water, alcohol, ether, vaseline and oils in general. It is the active odorous ingredient of the Tonquin bean (Tonca or Tonco bean), the seeds of at least two species of *Dipteryx* (N. O. *Leguminosæ*) in which it occurs up to 3 per cent. Coumarin possesses the characteristic odour of the Tonca bean, in which it was discovered in 1825 by Boullay (*Jour. de Pharm.*, xi., p. 480). It also occurs naturally in abundance in the dried leaves of *Liatris odoratissima* (deer's tongue, hound's tongue), an herbaceous plant common in North Carolina, 1 lb. of leaves yielding from 1½ to 2½ drachms of coumarin. It has also been found in the following plants:—

Angræcum fragrans
Myroxylon Pereiræ
Cevatopetalum apetalum
Ataxia Horsfeldii
Cinna arundinacea
Hierochloa alpina
„ *australis*
„ *borealis*
Milium effusum
Adiantum pedatum
„ *peruvianum*
„ *trapesiforme*
Drymaria Wildenovi
Phœnix dactylifera
Aceras Winthrophora
Nigritella angustifolia
Orchis fusca
Herniaria glabra
Ruta graveolens
Alyxia stellata
Asperula odorata
Galium trifolium
Liatris spicata
Prunus Mahaleb
Meliotus officinalis
„ *hamatus*
„ *albus*
„ *leucanthus*
„ *altissimus*
Ageratum mexicanum
Copaifera Salikounda
Trifolium Melilotus
Anthoxanthum odoratum

Coumarin was first produced synthetically by Perkin (*Chem. Soc. Journ.*, xxi., pp. 53, 181). He made it by heating salicylic aldehyde $C_6H_4(OH)^1(COH)^2$, acetic anhydride and sodium acetate. The whole solidifies to a crystalline mass, from which, on treatment with water, an oil separates containing coumarin and aceto-coumaric acid. This acid on heating is decomposed into acetic acid and coumarin, so that the product of distillation is principally coumarin.

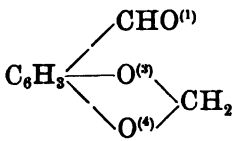
Coumarin is sometimes adulterated with acetanilide, which should always be looked for; the ease with which it yields aniline, on heating with potash solution, renders it very easy of detection. Some samples, otherwise pure, contain traces of unaltered salicylic aldehyde, which is revealed by the odour.

Synthetic coumarin is largely used in the place of Tonca beans, and forms an extremely useful substance for fixing other odours. Traces of fixed oil are useful in coumarin mixtures, as the coumarin odour appears to become more fixed in this way. Foin coupé, or new-mown hay, is a favourite perfume in which coumarin is the chief ingredient. The following table of solubilities of coumarin in alcohol of various strengths and in water has been compiled by Schimmel & Co.:—

100 parts of Alcohol		at 0° C.	at 16-17° C.	at 29-30° C.
Of 90 volume per cent.	dissolve	7·1 parts	13·7 parts	42·5 parts
,, 80 ,,		6·0 ,,	12·3 ,,	38·3 ,,
,, 70 ,,		4·4 ,,	9·1 ,,	26·0 ,,
,, 60 ,,		3·2 ,,	6·0 ,,	16·0 ,,
,, 50 ,,		1·7 ,,	3·4 ,,	8·9 ,,
,, 40 ,,		0·7 ,,	1·5 ,,	3·9 ,,
,, 30 ,,		0·3 ,,	0·6 ,,	1·7 ,,
,, 20 ,,		0·2 ,,	0·4 ,,	0·8 ,,
,, 10 ,,		0·15 ,,	0·25 ,,	0·5 ,,
100 parts of water		0·12 ,,	0·18 ,,	0·27 ,,

For further details of the chemistry of coumarin and its allies, the reader should consult any advanced text-book of organic chemistry.

Heliotropin.—This body, also known as piperonal, is a white crystalline compound possessing a powerful odour of heliotrope. It is the methylene ether of protocatechuic aldehyde, of the constitution—



The source from which it was originally made is the base piperine $C_{17}H_{19}NO_3$. Ground pepper, preferably white Singapore pepper (which contains up to 9 per cent. of the alkaloid), is mixed with slaked lime and water, and the whole evaporated to dryness on a water bath. The dry mass is then extracted with ether, which deposits the piperine on evaporation; or the pepper may be exhausted with alcohol, and the alcohol recovered. The semi-solid residue is mixed with potash solution, and the insoluble powder left is washed with water and recrystallised from alcohol, when the piperine is obtained nearly pure. When boiled with solution of caustic potash in alcohol, the base is converted into potassium piperate, which on oxidation with potassium permanganate yields heliotropin. The heliotropin of commerce, however, is manufactured by the oxidation of safrol. This body (*q.v.*) and its isomer isosafrol yield large quantities of heliotropin on oxidation with potassium permanganate or chromic acid.

To prepare heliotropin from isosafrol (which results from the isomerisation of safrol with alkalies), 5 parts of isosafrol are treated with a solution of 25 parts of potassium bichromate, 38 parts of concentrated sulphuric acid, and 80 parts of water. The reaction product is steam distilled and

the distillate is extracted with ether, and the heliotropin obtained is purified by means of alkaline bisulphite in the usual manner.

Heliotropin melts at 37°, but its perfume is injured by exposure to a temperature several degrees below this, and it should always be stored in cool dark places. In very hot weather the stock may with advantage be kept dissolved in alcohol, ready for use. This perfume is improved by blending it with a little coumarin or vanillin, or with bergamot, lemon or neroli oil. Attention should be drawn to the fact that the fancy perfumes whose names resemble heliotrope are usually mixtures of heliotropin—the cheaper ones being chiefly acetanilide, the more expensive ones containing vanillin or coumarin.

The intelligent perfumer, however, will always prefer to use the pure definite compound, heliotropin, and mix it according to his taste. In this, as in the case of many synthetic perfumes, fancy names are merely devices by which extra profits may be obtained.

The price of this product per lb. has regularly fallen since it was introduced into commerce. The following table shows the average price since 1880:—

	Per lb.		Per lb.
1880 . . .	£70	1890 . . .	£7
1881 . . .	47	1891 . . .	5 15s.
1882 . . .	31	1892 . . .	4 15s.
1883 . . .	21	1893 . . .	53s.
1884 . . .	21	1894 . . .	43s.
1885 . . .	14	1895 . . .	28s.
1886 . . .	12	1896 . . .	24s.
1887 . . .	11	1897 . . .	17s.
1888 . . .	8 10s.	1898 . . .	16s.
1889 . . .	8	1906 . . .	8s.

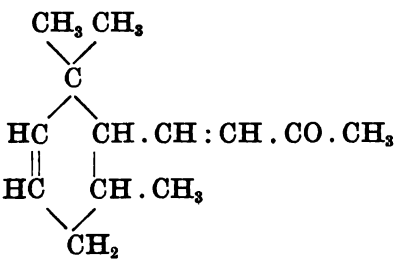
Aubépine, or *Hawthorn*.—The odour of May blossom is fairly well reproduced by anisic aldehyde, and the pure aldehyde is the basis of all hawthorn perfumes, the various

fancy preparations being preparations of this compound. Chemically anisic aldehyde is the methyl ether of *para*-oxybenz-aldehyde, of the constitution $C_6H_4(OCH_3)^1(CHO)^4$. It can be prepared from phenol by a series of reactions, or more easily by oxidising aniseed oil. The aldehyde is obtained by gently warming the oil for about an hour with three times its volume of nitric acid (specific gravity 1·1), and separating the heavy oil so formed, and washing it with potash solution. The crude oil is agitated with a warm concentrated solution of sodium bisulphite, with which the aldehyde combines, and the resulting crystalline magma is washed with alcohol and pressed in blotting paper, and dissolved in warm water. Excess of sodium carbonate is added, when the aldehyde is liberated and floats on the surface of the liquid. It can be further purified by distillation. When pure, anisic aldehyde is a liquid of characteristic hawthorn odour, of specific gravity 1·126 at 15°, boiling at 246° to 248°, and solidifying to a crystalline mass when cooled to a low temperature, melting again at – 4°. By oxidation in the air it is easily changed to anisic acid, which is of no value as a perfume, so that it should be stored in well-filled bottles. It is a very pleasant perfume, and blends exceptionally well with oils of the *Citrus* family, such as orange or petit-grains.

Ionone.—In 1893, after many years of patient research, Tiemann and Krüger succeeded in artificially preparing the artificial violet perfume which they termed ionone. The chemical relationships of this body are so interesting and important that Tiemann's work is here abstracted fairly fully.

The characteristic fragrance of the violet is also possessed to a considerable extent by dried orris root (iris root), and believing, although apparently erroneously, that both substances owed their perfume to the same body, Tiemann and Krüger used oil of orris for their experiments, instead of oil of violets, of which it was impossible to obtain a sufficient

quantity. The root was extracted with ether, the ether recovered, and the residue steam distilled. The non-volatile portion consists chiefly of resin, irigenin, iridic acid and myristic acid, whilst the volatile portion consists of myristic acid and its methyl ester, oleic acid, oleic anhydride, oleic esters, and the characteristic fragrant body which they termed irone. Irone has the formula $C_{13}H_{20}O$, and is an oil scarcely soluble in water, readily so in alcohol, boiling at 144° under a pressure of 16 mm., and of specific gravity ·939 at 20°. Its index of refraction is 1·50113, and it is dextro-rotary. The smell of this oil is quite unlike violets when in concentrated form, but if diluted, resembles them to some extent. It forms a crystalline oxime $C_{13}H_{20}N:OH$ melting at 121·5°. Irone is clearly a methyl ketone, probably of the constitution—

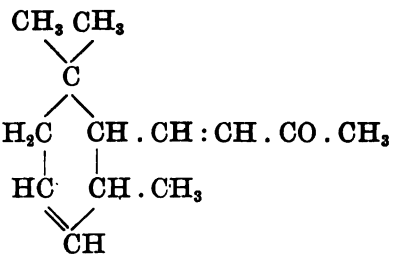


In order to attempt to synthesise irone, experiments were made which finally led to the condensation of citral with acetone, in the presence of alkalies. Irone was not obtained, but an isomer, which Tiemann called pseudo-ionone, as follows:—

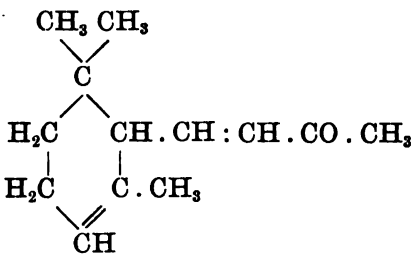
$$C_{10}H_{16}O + (CH_3)_2CO = C_{13}H_{20}O + H_2O.$$

Pseudo-ionone is an oil, boiling at 143° to 145° at 12 mm., of specific gravity ·8984, and refractive index 1·53346. If pseudo-ionone be heated with dilute sulphuric acid and a little glycerine, it is converted into another isomeric ketone, the now well-known ionone $C_{13}H_{20}O$. This substance was described as boiling at 126° to 128° at 12 mm., and has a specific gravity

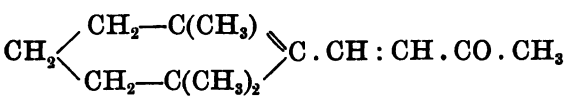
·9351 and refractive index 1·507, and is optically inactive. It has a characteristic violet odour, and at the same time recalls the vine blossom. Tiemann originally assigned to this body the formula—



But further researches on the chemistry of citral caused him later to support the formula—



Barbier and Bouveault, however (*Comptes Rendus*, 1897, p. 1308), assign to it the unlikely formula—



Tiemann later succeeded in resolving ionone into two isomeric compounds, which he terms *α*-ionone and *β*-ionone. Tiemann and Krüger obtained ionone by heating pseudo-ionone with dilute sulphuric acid. De Laire, using strong acid, obtained a quite similar body, but one which yielded different derivatives. This body is the original *iso*-ionone, or, as it is now called, *β*-ionone. *α*-Ionone is prepared from the commercial product by converting it into the

crystalline oxime, which is recrystallised from petroleum, and regenerating the ketone by means of dilute sulphuric acid, when *a*-ionone results. It boils at 123° to 124° at 11 mm., and 134° to 136° at 17 mm. It has a specific gravity ·932 and refractive index 1·4980. The oxime melts at 89° to 90°, and the semi-carbazone at 107° to 108°. *β*-Ionone is obtained from the commercial mixture by means of the semi-carbazone, which crystallises more readily than the corresponding derivative of the *a*-ketone, and can thus be separated. It boils at 127° to 129° at 10 mm., and has a specific gravity ·946 and a refractive index 1·521. The oxime is an oil, and the semi-carbazone melts at 148° to 149°. For further details of the chemistry of these bodies the original papers should be consulted (*Berichte*, xxvi., p. 2675; xxxi., pp. 808, 867).

Some of the most important modern work, which has led to good practical results, on the ionone question, is that of Dr. Philippe Chuit. Recognising the distinct differences between *a*-ionone and *β*-ionone from a perfumer's point of view, Chuit has devoted considerable time to devising practicable methods for their separation. The chief constituent of the ionone of commerce is *a*-ionone. By the use of concentrated sulphuric acid in the cold, the principal isomerisation product of pseudo-ionone appears to be *β*-ionone, and under the name violettone this product was put on the market. Numerous patents have been taken out for the preparation of the separate ionones, which need not be here discussed. Although ionone does not readily combine with alkaline bisulphite, yet it does so by prolonged boiling with the solution of bisulphite, a discovery made by Tiemann and utilised by him to remove impurities from crude ionone. Further, it was shown that the hydrosulphonic compound of *a*-ionone crystallised more readily than that of *β*-ionone, whilst the corresponding compound of *β*-ionone was the more easily decomposed by a current of steam. These facts constituted

a step towards the effectual separation of the isomeric ionones.

It has been proved that whilst concentrated sulphuric acid at a low temperature caused isomerisation of pseudo-ionone, so that the resulting product consists chiefly of β-ionone. But the use of phosphoric, hydrochloric and hydrobromic acids at low temperatures yields chiefly α-ionone.

In conjunction with Bachofen, Chuit has devised a method for separating the isomeric ionones depending on the following facts. The method is based on the insolubility of the sodium salt of the hydrosulphonic compound of α-ionone in the presence of sodium chloride, whilst the corresponding β-compound remains in solution. If sodium chloride be added to a hot solution of the hydrosulphonic compounds, separation of the α-salt takes place slowly as the solution cools, and the salt crystallises in fine white scales, which can be recrystallised from hot water. The β-compound remains in solution.

As an example of the efficacy of this separation the following is given: 5 grammes of α-ionone and 5 grammes of β-ionone were boiled with bisulphite solution for four and a half hours. To the solution, measuring 165 c.c., 40 grammes of sodium chloride were added. On cooling and standing, 11 grammes of moist crystals were obtained, which on decomposing in the usual manner, by caustic soda solution, yielded on steam distillation 5 grammes of α-ionone. The β-ionone was recovered from the mother liquor with a trifling loss.

The composition of the ordinary hydrosulphonic sodium compound of α-ionone is, according to Chuit,

$$(C_{13}H_{21}O \cdot SO_3Na \cdot)_2 + 3H_2O,$$

whilst that of β-ionone is $C_{13}H_{21}O \cdot SO_3\,Na + 2H_2O$.

From the point of view of practical perfumery, Chuit points out that the possession of the two pure isomers enables perfumers to produce numerous shades of violet perfume, with characteristic and distinct odours. α-Ionone has a

sweeter and more penetrating odour, rather resembling orris than violets, whilst β-ionone is said to more closely resemble the true fresh violet flower.

Patents covering the separation of the ionones are numerous.

The following is a copy of the provisional and complete specifications provided by the original patentee. The patent has now expired. Further examination of the bodies in question has shown that a few unimportant details require correction :—

Provisional Specification.—I, Johann Carl Wilhelm Ferdinand Tiemann, member of the firm of Haarmann & Reimer, of Holzminden, residing at Berlin, Germany, do hereby declare the nature of this invention to be as follows :—

I have found that a mixture of citral and acetone, if it is subjected, in the presence of water, for a sufficiently long time to the action of hydrates of alkaline earths or of hydrates of alkali metals, or of other alkaline agents, is condensed to a ketone of the formula $C_{13}H_{20}O$. This substance, which I term "Pseudo-ionone," may be produced for instance in shaking together for several days equal parts of citral and acetone with a solution of hydrate of barium, and in dissolving the products of this reaction in ether.

The residue of the ether solution is fractionally distilled under a reduced pressure and the fraction is collected, which boils under a pressure of 12 mm. at a temperature of from 138° to 155° C., and from it the unattacked citral and unchanged acetone and volatile products of condensation are separated in a current of steam, which readily carries off these bodies.

The product of condensation remaining in the distilling apparatus is purified by the fractional distillation *in vacuo*. Under a pressure of 12 mm. a liquid distils off at a temperature of from 143° to 145° C. This product of condensation which I term "Pseudo-ionone" is a ketone readily decomposable by the action of alkalies. Its formula is $C_{13}H_{20}O$, its index of refraction is n D = 1·527, and its specific weight 0·904.

The pseudo-ionone has a peculiar but not very pronounced odour; it does not combine with bisulphite of sodium as most of the ketones of the higher series, but, in other respects, it possesses the ordinary characteristic properties of the ketones, forming, in particular, products of condensation with phenylhydrazine, hydroxylamine and other substituted ammonias.

Although the odour of the pseudo-ionone does not appear to render it of great importance for its direct use in perfumery, it is capable of serving as raw material for the production of perfumes, the pseudo-ionone being converted by the action of dilute acids into an isomeric ketone, which I term "Ionone," and which has most valuable properties for perfumery purposes. This conversion may be effected, for example, by heating for several hours in

an oil bath 20 parts of "pseudo-ionone" with 100 parts of water, 2·5 parts of sulphuric acid, and 100 parts of glycerine, to the boiling point of the mixture. The product resulting from this reaction is dissolved in ether, the latter is evaporated, and the residue subjected to the fractional distillation *in vacuo*. The fraction distilling under a pressure of 12 mm. at a temperature of from 125° to 135° C. is collected. This product may be still further purified by converting it by means of phenylhydrazine or other substituted ammonias into a ketone condensation product decomposable under the action of dilute acids.

The ketone derivatives of the pseudo-ionone are converted under similar conditions into ketone-derivatives of the ionone. The pure ionone corresponds to the formula $C_{13}H_{20}O$, it boils under a pressure of 12 mm. at a temperature of about 128° C., its specific weight is 0·935, and its index of refraction n D = 1·507.

The ionone has a fresh flower-perfume recalling that of violets and vines, and is peculiarly suitable for being used in perfumery, confectionery and distillery.

The ionone, when subjected at a higher temperature to the action of hydroiodic acid, splits off water and gives a hydrocarbon corresponding to the formula $C_{13}H_{18}$, boiling under a pressure of 12 mm. at a temperature of from 106° to 112° C. This hydrocarbon is converted by strong oxidising agents into an acid of the formula $C_{12}H_{12}O_6$, melting at a temperature of 214° C.

Complete Specification.—I, Johann Carl Wilhelm Ferdinand Tiemann, member of the firm of Haarmann & Reimer, of Holzminden, residing at Berlin, Germany, do hereby declare the nature of this invention, and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

I have found that a mixture of citral and acetone, if it is subjected in the presence of water for a sufficiently long time to the action of hydrates of alkaline earths or of hydrates of alkali metals, or of other alkaline agents, is condensed to a ketone of the formula $C_{13}H_{20}O$. This substance, which I term "Pseudo-ionone," may be produced, for instance, in shaking together for several days equal parts of citral and acetone with a solution of hydrate of barium, and in dissolving the products of this reaction in ether.

The residue of the ether solution is fractionally distilled under a reduced pressure and the fraction is collected, which boils under a pressure of 12 mm. at a temperature of from 138° to 155° C. and from it the unattacked citral and unchanged acetone and volatile products of condensation of acetone by itself are separated in a current of steam, which readily carries off these bodies.

The product of condensation remaining in the distilling apparatus is purified by the fractional distillation *in vacuo*. Under a pressure of 12 mm. a liquid distils off at a temperature of from 143° to 145° C. This product of condensation of citral with acetone, which I term "Pseudo-ionone," is a ketone readily decomposable by the action of alkalies. Its formula is $C_{13}H_{20}O$, its index of refraction is n D = 1·527, and its specific weight 0·904.

The pseudo-ionone has a peculiar, but not very pronounced odour; it does not combine with bisulphite of sodium as most of the ketones of the higher series, but in other respects it possesses the ordinary characteristic properties of the ketones, forming, in particular, products of condensation with phenylhydrazine, hydroxylamine and other substituted ammonias.

Although the odour of the pseudo-ionone does not appear to render it of great importance for its direct use in perfumery, it is capable of serving as raw material for the production of perfumes, the pseudo-ionone being converted by the action of dilute acids into an isomeric ketone, which I term "Ionone," and which has most valuable properties for perfumery purposes. This conversion may be effected, for example, by heating for several hours in an oil bath 20 parts of "pseudo-ionone" with 100 parts of water, 2·5 parts of sulphuric acid and 100 parts of glycerine, to the boiling point of the mixture.

The product resulting from this reaction is dissolved in ether, the latter is evaporated and the residue subjected to the fractional distillation *in vacuo*. The fraction distilling under a pressure of 12 mm. at a temperature of from 125° to 135° C. is collected. This product may be still further purified by converting it by means of phenylhydrazine or other substituted ammonias into a ketone condensation product decomposable under the action of dilute acids.

The ketone derivatives of the pseudo-ionone are converted under similar conditions into ketone-derivatives of the ionone. The pure ionone corresponds to the formula $C_{13}H_{20}O$, it boils under a pressure of 12 mm. at a temperature of about 128° C., its specific weight is 0·935, and its index of refraction n D = 1·507.

The ionone has a fresh flower-perfume recalling that of violets and vines, and is peculiarly suitable for being used in perfumery, confectionery and distillery.

The ionone, when subjected at a temperature surpassing 100° C. to the action of hydroiodic acid, splits off water and gives a hydrocarbon corresponding to the formula $C_{13}H_{18}$, boiling under a pressure of 12 mm. at a temperature from 106° to 112° C. This hydrocarbon is converted by strong oxidising agents into an acid of the formula $C_{12}H_{12}O_6$ melting at a temperature of 214° C.

Having now particularly described and ascertained the nature of this invention, and in what manner the same is to be performed, I declare that what I claim is:—

1. A new chemical product termed pseudo-ionone obtained by the reaction of citral upon acetone in the presence of alkaline agents and subsequent treatment of the products, substantially as described.

2. A new article of manufacture termed ionone suitable for perfumery and the like and having the characteristics hereinbefore set forth, obtained from pseudo-ionone referred to in the preceding claim, substantially as described.

3. The process for the production of the pseudo-ionone referred to in the first claim, consisting in the subjection of a mixture of citral and acetone to the action of an alkaline agent, and in purifying the product of this reaction,

extracted by means of ether, by fractional distillation, substantially as described.

4. The process for the production of the ionone referred to in the second claim, consisting in treating the pseudo-ionone referred to in the first claim or its ketone condensation products with phenylhydrazine or other ammonia derivatives, finally with acids, substantially as described.

The commercial product, as put on to the market, was originally a 10 per cent. solution of ionone in alcohol. This was due not only to the expensive nature of the product, but also to the fact that its odour is very intense, and when pure, not like that of violets. Ten grammes of this solution are sufficient to produce one kilo of triple extract of violets when diluted with pure spirit. But to-day 100 per cent. violet perfumes, such as the violettone, above mentioned, are regular commercial articles. The perfume is improved both for extracts and soaps by the addition of a little orris oil, but in the author's opinion the odour of ionone is not nearly so delicate as that of the natural violet, although far more powerful. The prices asked for it are very high, and in regard to this the following optimistic statement occurs in Messrs. Schimmel & Co's. report for October, 1894: "The opinion, which is frequently expressed, that the price of ionone solution will probably be reduced before long is not justified. It is not the intention of the manufacturers to depreciate the article without reason or necessity, a policy which can only meet with the approval of the maker of high-class perfumes, for whose use ionone is intended, and who cannot gain by seeing violet odour, like so many other preparations, brought down to the level of a vulgar scent for common people."

With regard to the practical use of ionone, which sometimes presents a difficulty to perfumers, Messrs. Schimmel & Co. write:—

"This beautiful article maintains its position in the front rank of preparations for perfumery, and will probably remain

without a rival among artificial perfumes for some time to come. Although the violet scent has long been a favourite perfume, its popularity has doubled through the invention of ionone, and it is not too much to say that the introduction of that body alone has made it possible to produce a perfect extract. Some of the leading European perfumers produce violet extracts which may be recommended as examples of excellence, and which have deservedly become commercial articles of the first importance. The inventors of ionone have earned the gratitude of the entire perfumery industry, and may be congratulated in turn upon the remarkable success of their invention.

"As we have already pointed out on a previous occasion, the preparation of a violet extract in which ionone is made to occupy its due position is not such an easy task as is often assumed; on the contrary, it requires a long and thorough application.

"To obtain a perfect result with ionone is an art in the true meaning of the word, and on that account no inexperienced hand should attempt it. We again and again lay stress upon this fact, because in our business we are constantly brought face to face with people who think that they can make a suitable violet extract by simply mixing alcohol with ionone solution. This view is quite wrong. The employment of ionone presupposes above everything else that the user is acquainted with the peculiarities of the article and knows how to deal with them. Again and again the uninitiated come to us with the complaint that ionone has no odour at all, or that it smells disagreeably, although as a matter of fact these objections are usually withdrawn upon closer acquaintance with the article. The assumptions in question are only due to a blunting of the olfactory nerves, or, more correctly, to a nasal delusion, which also occurs sometimes in the case of other flower odours and to which

people are known to be particularly liable when smelling freshly gathered violets.

"The principal thing in connection with the employment of ionone is to discover its proper degree of dilution. In its natural state the body is so highly concentrated as scarcely to remind one of violets. This is the reason why it was placed in trade in the form of a 10 per cent. solution, and not in its pure state. This form has proved an exceedingly useful one. In using it for extracts, powders, sachets, etc., the solution must be further diluted and fixed with some orris oil, civet and musk."

By using acetone homologues, homologous or reduced ionones are produced which have intense odours of a similar character.

The above remarks apply to the commercial product known as ionone. There are, however, numerous other patents in existence for the preparation of artificial violet oil. The complete specification of one of these reads as follows:—

I, Alfred Julius Boult, of 111 Hatton Garden, in the County of Middlesex, Chartered Patent Agent, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a process for manufacturing hitherto unknown oils having a violet scent.

Patents No. 8,736 of 1st May, 1893, and No. 17,539 of 18th September, 1893, describe the manufacture of ionone, which is an essential oil, boiling at 128° under 12 mm. pressure, and of specific gravity of 0·935. This oil is optically inactive.

The final product of the process according to the present invention is an oil boiling at 142° to 150° C. under 12 mm. pressure and of specific gravity of from 0·94 to 0·95. It differs from ionone by having when concentrated a very strong scent similar to that of sandalwood by producing a left-handed rotation of a polarised ray and by having when diluted a scent more closely approaching that of natural violets than does that of ionone.

Analysis shows that this oil consists of several ketones of the group $C_{13}H_{20}O$ of higher boiling points and greater density than those of ionone. These ketones are optically active, and both their existence and their artificial production have been hitherto unknown.

The process employed in carrying out this invention is as follows: A mixture of 1 to 1½ parts acetone (45 kg.), 1 part of lemon-grass oil (38 kg.), 1½

to 2 parts of alcohol (75 kg.), 1 to 2 parts of a concentrated lime-free solution of chloride of lime (75 kg.), to which is added a little of cobaltous nitrate (30 gr.) dissolved in water, is boiled during 6 to 18 hours at a temperature of 70° to 80° C. in a reflux cooling apparatus.

The alcohol and the excess of acetone are first distilled off and then an essential oil is obtained, which, after the first distilled portion (about 4 kg.) of specific gravity 0·88 has been removed, represents the stuff for producing artificial oil of violets. It is an essential oil with a boiling point of 155° to 175° at 12 mm. pressure (about 25 kg.).

This oil is heated at 110° C. with a solution of bisulphate of sodium of 11° Beaume (42 kg. for 360 litres of water) in a vessel with a mixing device until the samples distilled every day show that the first running, which has an unpleasant smell, has reached the density of 0·936. This happens after about 8 days (the first running being about 8 kg.).

The crude product (about 17 kg.) in the vessel is then purified by fractional distillation, all the bad-smelling parts being removed, so that finally there remains an oil of a density of 0·948 to 0·952 (15° C.) boiling at 142° to 150° C. under 12 mm. pressure.

The lightest portion of this oil has a specific gravity of 0·945 and boils at 142° C. under 12 mm. pressure; the largest portion of it, which has the pleasantest and strongest smell, boils at 149° C. and has a specific gravity of 0·953. Analysis has shown that both substances belong to the group of ketones $C_{13}H_{20}O$.

By using other ketones instead of acetone homologous substances may be obtained.

The product obtained by the above described process contains no ionone, for it contains no ingredient boiling at 128° C. under the pressure of 12 mm. and having a specific gravity of 0·935. The violet-like smell of the product obtained according to the present invention is the result of the presence of substances which are different from ionone, as their specific gravity and their boiling point are higher than those of ionone. The new product has the advantage that it can be manufactured in a very simple and economical manner, and as its smell is much more like that of real violets than is the smell of ionone, and as it is more constant and less volatile than ionone, it is much more suitable for artificial violet scent than the "ionone" which has hitherto been the only artificially made substance known for this purpose, and which is much more difficult to manufacture.

Having now particularly described and ascertained the nature of the said invention as communicated to me by my foreign correspondents and in what manner the same is to be performed, I wish it to be understood that I do not claim anything described and claimed in the Specifications of Letters Patent Nos. 8,736 and 17,539, A.D. 1893, granted to Johann Carl Wilhelm Ferdinand Tiemann, but I declare that what I claim is:—

1. As an article of manufacture an essential oil having the smell of violets boiling at 142° to 150° C. under a pressure of 12 mm. and of a specific gravity of 0·948 to 0·952 (15° C.).

2. A process for the manufacture of hitherto unknown oils having the smell of violets, which oils have a higher boiling point and higher specific gravity than ionone.

3. A process for the manufacture of hitherto unknown oils boiling at 155° to 175° C. under the pressure of 12 mm., which can be converted into violet-smelling oils of higher specific gravity and higher boiling point than those of ionone by being boiled with different substances, such, for instance, as bisulphate of sodium.

4. The manufacture of homologous substances by using other ketones instead of acetone.

5. A process for the manufacture of artificial essence of violets consisting in causing lemon-grass oil, alcohol, acetone, and concentrated solutions of salts of hypochlorous acid to react on one another at the boiling temperature.

6. Process for manufacture of artificial essence of violets consisting in causing lemon-grass oil, alcohol, acetone, and concentrated solutions of salts of hypochlorous acid to react on one another at a boiling temperature, cobaltous nitrate being added if desired.

The author is indebted to Messrs. Fritzsche & Co. for the following information, in regard to ionone perfumes.

They state that their invention relates to the preparation of cyclic ketones of the same group as ionone, but with higher boiling points and higher specific gravity. They claim to have proved that, corresponding to the pseudo-ionone of the patent No. 8,736 of 1893, which distils at 143° to 145° (12 mm.), and which finally gives the ketone ionone of boiling point 126° to 128° (12 mm.), and specific gravity 0·935 (20° C.), there exists also an iso-pseudo-ionone which distils at 149° to 151° (12 mm.), and which gives iso-ionone of boiling point 133° to 135° (12 mm.) and specific gravity 0·943 (20° C.), and further that there exists still another iso-pseudo-ionone which distils at 157° to 160° (12 mm.), and which gives a cyclic ketone of boiling point 142° to 146° and specific gravity 0·960 (20° C.).

They also claim that large quantities of iso-pseudo-ionone are formed in the process of Tiemann's patent, and which can be separated by distillation, coming over at a higher temperature than the ordinary pseudo-ionone.

Other very important and modern patents on this subject

are No. 18,333 of 13th September, 1901, and No. 705 of 19th January, 1903, both taken out in this country.

Artificial Musk.—The chemistry of natural musk, the preputial secretion of the musk deer, *Moschus moschiferus*, is not well defined, and attempts to prepare artificial musk have not been made on the basis of any knowledge of the constitution of the natural perfume. For accounts of the materia medica and commerce of this natural product, works on materia medica should be consulted. A useful account will be found in vol. i. of Sawyer's *Odorographia*.

For many years attempts have been made to artificially imitate the odour of musk. To a certain extent successful experiments were made by Margraff and Elsner (*Journ. für Praktische Chemie*, 1842). Rough pieces of amber, ground to powder and mixed with sand, are distilled in an iron retort, the oil which distils over is separated from the fœtid liquor and succinic acid which accompanies it, and after being rectified at a gentle heat with about six times its volume of water, is gradually added to and digested with 3¼ parts by weight of fuming nitric acid, artificial cold being employed to prevent any portion of the oil carbonising. A resinous matter of a yellowish colour forms, which, after being dried, is the product which is required. It is said to be also formed by digesting for ten days an ounce of fœtid animal oil, obtained by distillation, and half an ounce of nitric acid, then adding a pint of rectified spirit, and digesting for one month. Another artificial musk has been patented in England (No. 18,521, 18th Dec., 1888) by Schnaufer & Hupfeld, of Frankfurt. The specification of this patent states that "three parts of metaxylol, two parts of isobutyl alcohol, and nine parts of chloride of zinc are heated in a digestor to from 220° to 240°, until the pressure, which at the commencement is from 25 to 29 atmospheres, sinks to below 6 atmospheres. The resulting hydrocarbon,

corresponding to the formula $C_{12}H_{18}$, is collected, and the fraction which distils over at from 190° to 230° is nitrated with HNO_3, or with HNO_3 and H_2SO_4, whilst being cooled. The product of the reaction is poured into water, whereupon a reddish-brown oil separates, which is washed several times with alkaline water. The formula of this oil is $C_{12}H_{17}NO_2$, and in a concentrated condition it possesses a sweet smell, whilst in a dilute solution it gives off a penetrating and enduring musk-like odour."

The complete specification states that "aromatic hydrocarbons containing the iso-propyl, iso-butyl, or iso-amyl group, on treatment with fuming nitric acid or a mixture of strong nitric acid (40° to 44° B.) and sulphuric acid (66° B.), produce derivatives which, in very dilute alcoholic solution, furnish a liquid possessing an odour resembling tincture of musk in the highest degree". Only one example of the process is given in the provisional specification, but of course the process may be carried out with the other well-known homologues. "The hydrocarbons may be produced in the ordinary way, but we produce them by the following operation. Toluene or xylol is heated in a digestor with iso-propyl or iso-butyl, or iso-amyl alcohol in molecular quantities, with the addition of from four to five times the quantity of chloride of zinc, to the boiling point of the hydrocarbon, or to about 40° or 50° above the boiling point of alcohol, until the pressure, which at the commencement was equal to about 26 atmospheres, sinks to a little above 2 or 3 atmospheres. The product of the reaction is subjected to fractional distillation.

"By the above process the following hydrocarbons are obtained:—

1. From Toluene:—
   - Methylisopropyl-benzene.
   - Methylisobutyl- „
   - Methylisoamyl- „

2. From Xylol :—
Dimethylisopropyl-benzene.
Dimethylisobutyl- „
Dimethylisoamyl- „

"To produce the 'musk-substitute':—

"We add to the above-mentioned hydrocarbons, which during the operation should be kept thoroughly cool, a little more than the molecular quantity of fuming nitric acid or nitro-sulphuric acid. The acid should be gradually run in and the whole then allowed to stand undisturbed for from one to two hours, the resulting mass being then poured into water in order to get rid of the excess of acid. The well-washed substances thus obtained are then subjected to distillation by means of steam, whereupon simultaneously formed bodies, which smell like nitro-benzol and overpower the musk odour, readily distil over, whilst the pure substances remain behind."

The artificial musk which was the first to achieve marked success was that manufactured under the patent of Albert Baur (English patent No. 4,963 of 1889). The provisional and complete specifications of this patent are as follows :—

Provisional Specification.—I, Albert Baur of Gispersleben, in the Empire of Germany, Doctor, do hereby declare the nature of this invention to be as follows :—

The object of this invention is to produce a compound or material, or series of compounds or materials, having the properties of musk.

To this end I purpose to make a nitrated hydrocarbon of the $C_{11}H_{16}$ group and proceed as follows :—

Toluene is mixed with a haloid combination of butane and boiled with addition of chloride or bromide of aluminium. Water is added to the product and it is then distilled with steam, and that portion which distils over at a temperature between 170° and 200° C. is taken and treated with fuming nitric acid and fuming sulphuric acid. The resulting product is washed with water and crystallised from alcohol.

The product may be dissolved in alcohol, and on addition of a small quantity of ammonia or sal-ammoniac will exhibit all the essential properties of a tincture of musk.

Complete Specification.—I, Albert Baur of Gispersleben, in the Empire of Germany, Doctor, do hereby declare the nature of my invention and in

what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

The object of this invention is to produce a compound or material, or series of compounds or materials, having the properties of musk.

To this end I make a nitrated hydrocarbon of the $C_{11}H_{16}$ group and proceed as follows:—

Toluene is mixed with a haloid combination of butane and boiled with addition of chloride or bromide of aluminium. Water is added to the product and it is then distilled with steam, and that portion which distils over at a temperature between 170° and 200° C. is taken and treated with fuming nitric acid and fuming sulphuric acid. The resulting product is washed with water and crystallised from alcohol.

The product may be dissolved in alcohol, and on addition of a small quantity of ammonia or sal-ammoniac will exhibit all the essential properties of a tincture of musk.

For carrying the invention into practice, five parts of toluene are mixed with one part of butyl bromide, or butyl chloride or butyl iodide, and to these may be added gradually whilst boiling ¼ part of aluminium chloride or aluminium bromide; this results in the development of hydrobromic acid, or hydrochloric acid or hydriodic acid respectively, and a product of reaction is obtained from which by the action of steam the hydrocarbon $C_{11}H_{16}$ and unchanged toluene are distilled. By the admission of steam the hydrocarbon is carried along and may be obtained in a condenser as a colourless oil floating on the water. The oil removed and dried by means of chloride of calcium is fractionated, and in this manner the necessary hydrocarbon for the production of artificial musk is obtained, 100 parts of the former giving a like quantity of musk preparation. Three parts of fuming nitric acid of 1·52 specific weight and six parts of fuming sulphuric acid are mixed together, and to this mixture is carefully added whilst cooling one part of the hydrocarbon aforesaid. Each drop causes a violent reaction. As soon as all the hydrocarbon is added, the whole mixture is heated up to a temperature of about 100° C. After cooling, the nitro product is precipitated by pouring into cold water of about five to six times the volume, and is separated from superfluous acid by washing with cold water. The nitro product separates first as a heavy viscid oil, which after some time hardens into a firm crystalline substance.

The raw nitro product is then purified by recrystallisation from alcohol of 90 per cent. strength. The purified product crystallises out in yellowish-white needles, possessing a strong smell of musk.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

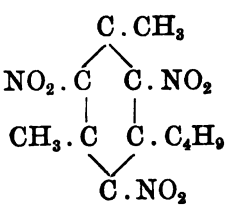
The process for producing artificial musk substantially as described.

The original scientific account of the preparation of this body stated (*Comptes Rendus*, cxi., p. 238) that *meta*-iso-

butyl toluene was heated on a water bath for twenty-four hours, with five times its weight of a mixture of sulphuric and nitric acids. The product was subjected to a repetition of the same treatment, so as to convert it into trinitro-butyl toluene, which crystallises from alcohol in white needles melting at 96° to 97°. It is insoluble in water, but soluble in organic solvents. Even in very dilute solutions this compound has a strong odour of musk, and for many purposes can replace the natural product. The homologues of isobutyl toluene behave similarly and trinitro-isobutyl metaxylene has an exactly similar odour. In a later communication (*Berichte*, xxiv., p. 2832) Baur stated that his previous view was incorrect, and that the "artificial musk" was the trinitro-derivative of *tertiary* butyl xylene, and not of isobutyl xylene, owing to the occurrence of an intra-molecular change during the reaction. Tertiary butyl xylene is easily prepared by the interaction of tertiary butyl chloride and xylene in the presence of aluminium chloride as follows:—

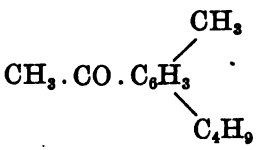
$$C_4H_9Cl + C_6H_4(CH_3)_2 = C_4H_9 . C_6H_3 . (CH_3)_2 + HCl.$$

The mono- and dinitro products have no musk odour, and therefore the nitration of the hydrocarbon should be carried as far as possible. The constitution of this artificial musk, or "xylene musk" as it is often called, is probably—

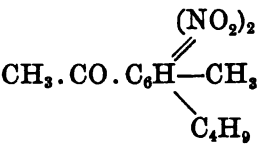


Still later (*Berichte*, xxxi., p. 1344), Baur has shown that if an acetyl group is introduced into the butyl toluene molecule, and the methyl ketone thus formed is nitrated, artificial musk (ketone musk) is produced. One part of butyl toluene,

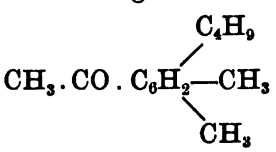
ten parts of carbon disulphide, and six parts of aluminium chloride are cooled in a flask and six parts of acetyl chloride are run in quickly. After distillation on a water bath, the residue is poured on to ice and treated in the usual manner. The acetyl derivative is obtained as an oil with a pleasant aromatic odour, boiling at 255° to 258°, of the formula—



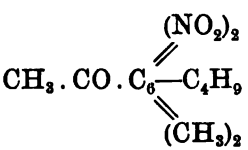
By nitrating this ketone a dinitro derivative—



is obtained in needles melting at 131°, and having a strong musk odour. In this compound one of the nitro groups of the original artificial musk, trinitro-butyl toluene, has been replaced by the acetyl group. Which group has been so replaced is uncertain. A quite similar body is obtained from butyl xylene, the resulting ketone—

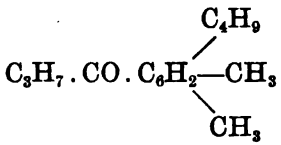


melting at 48°, and yielding a dinitro derivative—



melting at 136°, and having a strong musk odour. These bodies are known as "ketone musk". Instead of using acetyl chloride, either butyryl chloride or valeryl chloride

may be used, and higher homologues produced. Butyl-xylyl-propyl ketone—



melts at 50° and boils at 290°. It forms a dinitro derivative, melting at 128°, with a powerful musk odour. The corresponding butyl-xylyl-butyl ketone is an oil boiling at 185° to 190° at 14 mm., and its dinitro derivative melts at 151°, and has also a powerful musk odour. An error occurs in the abstracts of this paper in the *Chemical Society's Journal* (1898, p. 525), where the propyl and butyl groups have been rendered butyl and amyl respectively.

Under the name musk ambrene Messrs. Chuit, Naef & Co. prepare a nitrated derivative of the methyl ether of butyl-*meta*-cresylol, which has a characteristic odour and is far stronger in musk odour than either xylene or ketone musk.

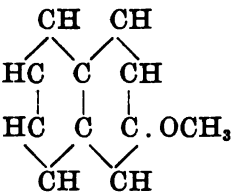
The use of artificial musk is fairly extensive for perfumery of a certain kind, where powerful odours are desired. It finds considerable employment in the scenting of toilet soaps, a little alkali improving its odour.

It will here be convenient to mention that by the distillation of musk, Schimmel & Co. have separated a small amount of an essential oil of which the principal odoriferous ingredient is a ketone of the formula $C_{15}H_{28}O$, or $C_{16}H_{30}O$. This body is termed muskone, and has a specific gravity 0·927, optical rotation − 10° and refractive index 1·4790. It forms a semicarbazone melting at 133° to 134°. It is therefore obvious that "artificial musk" (nitro-musk) is not in any way identical with the natural musk odour bearer.

Artificial Neroli.—There are two artificial neroli sub-

stitutes which are more or less common commercial articles. One of these is a crystalline product sold under the name of nerolin at about 1s. 6d. per ounce, whilst the other is a "synthetic neroli oil," sold at about 6s. per ounce.

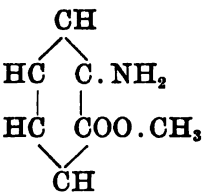
Nerolin crystals should be of a definite character, as this body is expected to be the pure compound—β-naphtol methyl ether, of the constitution—



This body is a white crystalline compound, melting at 70° and boiling at 294°. It can be prepared by heating 5 parts of β-naphtol with 5 parts of pure methyl alcohol and 2 parts of concentrated sulphuric acid for several hours to 125° under low pressure. This body was first introduced into commerce under the name Yara-yara, although the Yara-yara of commerce is now described as having an acacia odour. The corresponding ethyl ether $C_{10}H_7OC_2H_5$ melts at 37°, and boils at 274°, and has been introduced into commerce under the name "Bromelia". In some price-lists nerolin and Bromelia are given as synonyms. Its odour is not quite describable, and is incorrectly referred to that of pine-apples in older literature.

Synthetic neroli oil, being a mixture of various bodies (see *neroli oil*) is naturally much more variable in composition. Whilst the well-known alcohols geraniol and linalol, together with their acetic esters, enter into the composition of the oil, its characteristic odour is certainly due to other bodies; of these the best defined, the discovery of which was first announced by E. & H. Erdmann (*Berichte*, 1899, p. 1213), is the methyl ester of anthranilic acid. This

body is a crystalline solid, melting at 25° to a liquid oil, with a fine blue fluorescence, of specific gravity 1·168 at 15°, and boiling at 132° under a pressure of 14 mm. Its constitution is—



Anthranilic acid (*ortho*-amidobenzoic acid) was first prepared from indigo, but is now manufactured by reducing *ortho*-nitrobenzoic acid with tin and hydrochloric acid, or by oxidising aceto-*ortho*-toluidine with potassium permanganate, and boiling the resulting product with hydrochloric acid. The pure acid forms long needles melting at 144°. It is converted into its methyl ester by means of condensation with pure methyl alcohol in the presence of acids.

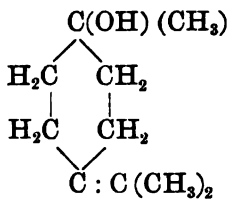
The artificial neroli oils of commerce are very uneven in value, as their composition is by no means constant.

Artificial Lilac. — The well-known body, terpineol $C_{10}H_{17}OH$, possesses an odour which, especially when the substance is diluted, more closely resembles lilac than any other flower. At the same time it recalls elder flowers and hyacinth, and is consequently used with other bodies as the basis of many artificial perfumes. It may here be advisable to emphasise that the practical perfumer should employ pure terpineol as the basis of his floral perfumes of this nature, as a little practice will soon enable him to reproduce the commercial products by the admixture of the proper quantity of other substances. Muguet is a favourite perfume, of a more or less pronounced lilac odour (although the name is merely the French equivalent of lily of the valley). A mixture of terpineol (90 per cent.) with palmarosa oil (10 per cent.) will

serve the purpose of this perfume. Syringol, or syringa oil, may be replaced by terpineol, if necessary with the addition of traces of various other oils. Lilacine and gardenia extract may be substituted by a mixture of terpineol and heliotropin (10 to 20 per cent.) with a trace of linalol or geraniol. In general lilac extracts, or "white lilac," may be regarded as solutions of terpineol, which are slightly modified by the addition of other perfumes, according to taste. For soap perfumery 1 per cent. of terpineol is sufficient, and the resulting soap is admirably perfumed. On account of its stability, neither heat, alkalies nor acids have any appreciable effect on this perfume, hence its utility in this branch of perfumery. For excellent results the following perfumes may be added. Oils of ylang-ylang, geranium, sandalwood or rose, or crystalline heliotropin. The latter body, however, does not stand the effects of heat.

Terpineol comes into commerce in two forms—the liquid and the crystalline, and although the latter is by far the more expensive, the former is of finer odour. Many commercial specimens have very poor odours and are by no means pure.

It appears more than probable that pure terpineol (see page 43) is a solid crystalline body, melting at 35° and boiling at 217°, at 760 mm. Its specific gravity at 20° in the solid state is ·9057. The liquid terpineol of commerce is in all probability merely terpineol with traces of impurities which prevent its crystallising. It is a viscous liquid, of specific gravity ·940 to ·945, boiling at 215° to 218°. It is optically inactive, but Semmler has prepared it in both optically active varieties by replacing the chlorine in both of the limonene monohydrochlorides, by the hydroxyl group. Baeyer has synthesised an *isomeric* terpineol, of similar odour, which occurs in crystals melting at 69° to 70°, and which almost certainly has the constitution—



Possibly ordinary liquid terpineol consists of a mixture of this terpineol and that of melting point 35°, with traces of impurities. (But see under "Terpineol".)

The ordinary method of preparing terpineol is from terpin-hydrate $C_{10}H_{20}O_2 + H_2O$. This body is prepared by (*for example*) the following process, described by Hempel (*Ann. Chem.*, xxx., p. 71): "Eight parts of oil of turpentine are mixed with two parts of alcohol and two parts of nitric acid (specific gravity = 1·25) in a flat basin. After a few days the liquid is poured off from the crystals which have already separated, and is neutralised with an alkali, after which another crop of crystals separates. The preparation only succeeds during cool weather, as in summer a resinous mass is usually obtained." Terpin-hydrate forms large, transparent monosymmetric prisms melting at 117°. From this body Wiggers obtained by the action of hydriodic acid a compound which was investigated by List, and named by him *terpineol*. It was described as a colourless oil with a pleasant odour of hyacinths. Tilden (*Jour. Chem. Soc.*, xxxiii., p. 247, and xxxv., p. 287) showed that this was a mixture of at least one terpene with an oxygenated body, and Wallach (*Annalen*, ccxxx., p. 251) showed that it was a mixture of the terpenes dipentene, terpinene and terpinolene with the oxygenated body terpineol $C_{10}H_{17}OH$.

There is on the market also a body called terpinolene, which is not the pure terpene of this name, but a mixture of the terpenes obtained when manufacturing terpineol, and which is offered as a cheap lilac perfume. It

can scarcely be recommended, however, as its odour is very weak.

Terpineol is prepared in various ways. According to Voiry and Bouchardat, terpin-hydrate is heated with very dilute sulphuric acid (·1 per cent.), and the resulting terpineol is purified by crystallisation and fractionation. Wallach (*Annalen*, ccxxx., p. 264) recommends treating twenty-five parts of terpin-hydrate with fifty parts of phosphoric acid (specific gravity = 1·12). The resulting product is steam-distilled and fractionated. Flawitzky (*Berichte*, xii., p. 2354) recommends allowing one part of French turpentine oil to stand for twelve hours, with half its weight of concentrated sulphuric acid and one and a half times its weight of 90 per cent. alcohol. Renard recommends the electrolysis of a mixture of alcohol, turpentine and sulphuric acid. Bertram and Walbaum have patented the following method (German patent, 67,255). Two kilogrammes of acetic acid are mixed with 50 grammes of sulphuric acid and 50 grammes of water. Into the mixture, which should not be allowed to rise above 50° C., 1 kilogramme of rectified turpentine oil is poured, in portions of 200 grammes at a time. After cooling and standing the liquid is diluted with water and shaken with soda solution. The product consists of terpinene and terpineol esters, which are separated by fractional distillation. The esters, on treatment with alcoholic potash, yield terpineol.

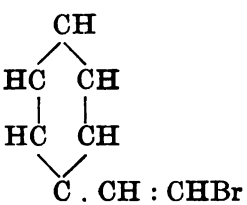
Ertschikowsky's process consists of allowing 450 grammes of pinene to stand for a day with 900 grammes of acetic acid and 100 grammes of zinc chloride. The reaction product contains several bodies, amongst which is terpineol acetate, which on saponification yields solid terpineol.

In order to keep this perfume at its best it should be stored in well-corked, dark-coloured bottles.

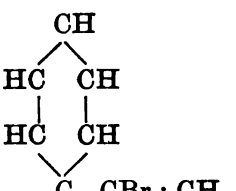
Artificial Hyacinth.—Several artificial hyacinth oils are on the market which are fairly good imitations of the natural

perfume. As has been already mentioned, terpineol has a certain resemblance, although not a very close one, to this perfume, hence it forms an ingredient in most of the commercial "hyacinth extracts," etc. The artificial oils, however, contain several bodies of powerful odour, but their exact composition is kept as a trade secret, and their analyses have not been published. The following bodies, however, in addition to terpineol, have odours recalling hyacinths, and doubtless enter into the composition of the artificial oils:—

α-Chlorstyrolene and *α*-bromstyrolene are both oils of characteristic hyacinth odour. Styrolene or phenyl-ethylene $C_6H_5 . CH : CH_2$ is a hydrocarbon occurring in storax, but it can easily be produced by several synthetic reactions, such as by the action of alcoholic potash on bromethyl benzene, $C_6H_5 . CH_2 . CH_2Br$. It is best obtained by acting with soda solution on *β*-bromhydrocinnamic acid. It is a mobile, strongly refracting liquid of agreeable odour. It is optically inactive, boils at 144°, and has a specific gravity ·925 at 0°. It yields two series of derivatives in which the hydrogen of the side chain suffers replacement. For example, the bromine derivatives have the constitutions—



α-bromstyrolene.

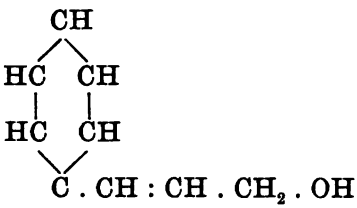


β-bromstyrolene.

It is remarkable that the *β*-bromine and chlorine derivatives are oils which have a penetrating odour, producing a copious flow of tears; the *α* derivatives are oils with a sweet, hyacinth-like odour. *α*-Chlorstyrolene boils at 199°, and *α*-bromstyrolene melts at 7° and boils at 220°. The derivatives here

described as α are designated ω in Beilstein, while the derivatives here described as β are described as α by that authority.

Styryl alcohol $C_9H_{10}O$, also known as cinnamyl alcohol or cinnyl alcohol or styrone, has a powerful odour, recalling hyacinths. It has the constitution—



and is obtained by saponifying its cinnamic ester, styracine, which occurs in storax and balsam of Peru. It forms shining needles, melting at 33° and boiling at 250°.

Benzyl alcohol $C_6H_5 . CH_2 . OH$ is an aromatic body in which the odour of bitter almonds and hyacinths may be traced. It is easily produced by various reactions, amongst which is the action of water on benzyl chloride. The latter body is obtained by the action of chlorine on boiling toluene, and is converted into benzyl alcohol by boiling with water and lead hydroxide, or even with water alone:—

$$C_6H_5CH_2Cl + H_2O = C_6H_5CH_2OH + HCl.$$

Pure benzyl alcohol is a liquid of specific gravity 1·0628 at 0°, or 1·0507 at 15°, and boils at 206°.

Artificial hyacinth oil no doubt contains some or all of these bodies with possibly some aromatic esters in addition.

Artificial Lemon Oil.—There are on the market preparations which bear the label "synthetic oil of lemon (terpeneless)" and which possess a strong lemon odour. The term synthetic is, in the author's opinion, quite unjustifiable, as samples he has examined consist chiefly of lemon-grass citral, which is not a synthetic product. Citral in a diluted form has been strongly recommended as a substitute for lemon oil by Messrs. Schimmel & Co., who in their report

for October, 1896, say that 75 grammes of citral would suffice as a substitute for 1 kilo of oil of lemon. But its flavour is somewhat wanting in the degree of freshness characteristic of good lemon oil; but this slight deficiency is fully neutralised by an addition of lemon oil. Therefore citral is now generally used in combination with oil of lemon. The most approved proportion is 100 grammes of citral to 1,400 grammes of oil of lemon. This is equivalent in odoriferous strength to 3 kilogrammes of oil of lemon.

"Fifteen grammes of the mixture are sufficient for making 1 hectolitre of lemon liquor, and this remains clear even if it contains only 30 per cent. of alcohol. For making lemon syrup to be used for lemonades, 20 to 25 grammes are sufficient for 100 kilos of syrup. When the use of citral is preferred without the addition of oil of lemon, the following solution deserves the preference: 75 grammes of citral and 925 grammes of alcohol (95 per cent.). This equals 1 kilogramme of oil of lemon in odoriferous power."

This statement is in the author's opinion hardly correct. Citral is in no sense a substitute for oil of lemon. Not only does it lack the fine aroma which the presence of aromatic esters such as geranyl acetate, and other as yet unidentified bodies give to true lemon oil, but it is very difficult to remove from it the last traces of the lemon-grass odour and taste, which by no means improve it for the purpose for which it is recommended. Further, the fact that the solution of citral in alcohol is admitted to lack the characteristic lemon freshness, makes it exceedingly illogical to say that the deficiency is neutralised by adding true lemon oil. What actually happens is that the true lemon oil covers the poor odour of the artificial mixture, but merely gives to the whole the average value of the ingredients. Users of lemon oil should not be deceived, however, by the term "synthetic oil of lemons". If a cheap substitute is wanted it should be bought

under the name of citral, and the individual user must then decide for himself whether it suits his purpose.

Artificial Rose Oil.—Although numerous "artificial" and "synthetic" rose oils are listed by various firms, there is nothing which quite resembles the natural otto of roses. These artificial ottos or oils of roses are, as a rule, merely clumsy imitations of the natural product. The absurdity of some of them is accentuated when they not only imitate the true oil in odour but also in appearance, for the crystalline stearoptene of natural oil of roses is quite odourless, but yet some "artificial" oils are made to solidify at the same temperature as the genuine oil. Indeed in most cases artificial oils of roses may be described as quite unscientific attempts at artificial perfumery. The two best defined constituents of oil of roses are the alcohols geraniol and citronellol, and these bodies with a trace of their acetic esters will produce as good an "artificial oil of roses" as may be. A little genuine oil of roses is frequently added to make the substitute a little more passable. The chemistry of geraniol and citronellol has already been dealt with at some length, but the following details of the practical methods of their preparation will not be out of place in the present chapter.

Geraniol $C_{10}H_{17}OH$ (see page 52) has been the subject of several patents. Amongst these may be classed that for the preparation of "rhodinol" from geranium and pelargonium oil (German patent 80,007). To prepare rhodinol the oil is distilled under reduced pressure (14 mm.), and the fraction 120° to 130°, consisting of impure rhodinol, is heated in an autoclave with acetic anhydride, and the resulting esters are fractionated. The fraction 127° to 132°, consisting of the acetic ester of "rhodinol," is saponified with alkali, and the resulting oil is fractionated *in vacuo*. The portion distilling between 120° and 125° is an oily colourless fluid with a rose-like odour, and is the commercial rhodinol.

A patent was taken out for the preparation of geraniol from citronella oil by Schimmel & Co. (German patent 76,435). Here either the citronellic aldehyde is removed by means of alkaline bisulphite or polymerised by alkalies, and the geraniol obtained by fractional distillation.

Jacobsen's method, which is adopted for the purification of geraniol, depends on the fact that geraniol yields a crystalline compound with calcium chloride. The geraniol containing fractions of the oil are well rubbed with freshly fused calcium chloride and the mixture allowed to stand *in vacuo* at a low temperature. The compound $2C_{10}H_{18}O \cdot CaCl_2$ crystallises out and is washed with absolute ether and decomposed with water, when pure geraniol is set free. The geraniols of commerce vary very much in odour (and therefore in purity), but the best varieties do not possess anything like so fine an odour as rose oil. It is customary, too, to distil geraniol over various flowers, such as roses, mignonette, or hyacinths, and sell the resulting perfume as rose-geraniol, mignonette-geraniol, etc. These perfumes are of much more delicate and finer odours than ordinary geraniol. Citronellol occurs associated with geraniol, and unless removed specially, always occur in the alcoholic bodies separated from the various geranium oils. The compounds described under the names of rhodinol, réuniol and roseol appear to be mixtures of both alcohols.

Mentho-citronellol (*q.v.*) $C_{10}H_{19}OH$, prepared by Wallach (*Ann. Chem.*, cclxxviii., p. 302, and ccxcvi., p. 129), is possibly identical, possibly isomeric with citronellol. It has a strong rose odour. A body patented by Schering (German patent 96,657), and which is described under the name *di-methyl-heptadineol*, also possesses a strong rose odour. This body, which possesses the formula $C_9H_{16}O$, has a fair rose odour. It is prepared by a series of very complex reactions, but as the body has not much practical interest the reader is referred to

the original patent for the details. For other compounds existing in otto of roses, see under Oil of Roses. Dr. P. Chuit has succeeded in imitating several individual roses, such as the Marchal Niel, with marked success, by the use of artificial perfumes entirely. The composition of such oils is kept a trade secret.

Niobe Oil.—The synthetic perfume sold under this name is merely methyl benzoate $C_6H_5.COOCH_3$. It is a liquid of specific gravity 1·103 at 15°, and boils at 195° to 196°. It can be prepared by dissolving benzoic acid in excess of methyl alcohol CH_3OH, and saturating the solution with dry hydrochloric acid gas. The whole is warmed to 100° for a few hours, and then water is added, which throws out the oil which is purified by rectification.

Artificial Orchids.—The basis of the artificial orchid perfumes is amyl salicylate $C_6H_4(OH)(CO_2C_5H_{11})$. This ester has a marked perfume value and its odour is modified to taste by the addition of small quantities of other esters and alcohols.

Bergamiol.—This body, which is used as a substitute for bergamot oil, and which it resembles very fairly, is simply linalyl acetate $C_{10}H_{17}.C_2H_3O_2$ (*q.v.*). It is prepared by heating linalol with the calculated quantity of acetic anhydride for a few hours and distilling the resulting oil under reduced pressure after being washed with weak alkali. It is purified by rectification *in vacuo*.

Artificial Jasmin Oil.—The natural jasmin perfume is due to an essential oil (*q.v.*), but as this is both exceedingly delicate and expensive, it is generally extracted in the form of a pomade. There are, however, several brands of synthetic oil of jasmin on the market, the exact composition of which is kept secret. None of them are single compounds, but are mixtures of several odoriferous bodies which together reproduce the jasmin perfume very fairly. According to

Verley (*Comptes Rendus*, 30th Jan., 1899), the natural oil consists of about 10 per cent. of linalol and 90 per cent. of phenyl-glycol-methylene acetal. These results led to the taking out of a French patent for artificial oil of jasmin. Hesse and Müller deny the existence of the latter body in jasmin oil, or that it has a jasmin odour. They claim that benzyl acetate is the chief constituent of the oil, and they state that the average composition of the oil is as follows: benzyl acetate, 65 per cent.; linalyl acetate, 7·5 per cent.; benzyl alcohol, 6 per cent.; linalol, 16 per cent. About 5 per cent. of other odorous bodies occur, the nature of which is not given. As previously stated, secondary styrolyl acetate $C_6H_5 . CH (O . COCH_3) CH_3$ has a marked jasmin odour. Artificial jasmin oil is made on the basis of these researches, although probably small quantities of some bodies not generally known are added by the manufacturers. The chemistry of benzyl alcohol, linalol and linalyl acetate has already been referred to in detail. Benzyl acetate is a liquid of specific gravity 1·057, prepared by acetylating the alcohol. Its boiling point is 206°. Secondary styrolene acetate is an oil boiling at 217° to 220° prepared in the following manner. Ethyl-benzene $C_6H_5 . C_2H_5$ is prepared by heating benzene with aluminium chloride and ethyl bromide. By acting on this body with bromine at the boiling temperature of the liquid, β-brom-ethyl-benzene $C_6H_5 . CHBr . CH_3$ is formed, which by the action of silver acetate and acetic acid is converted into secondary styrolyl acetate $C_6H_5 . CH(O . COCH_3) CH_3$. The ketone, jasmone, has also to be considered in taking into account the odour value of this oil.

Artificial Cognac Oil.—Cognac oil, which is perhaps not an essential oil in the fullest sense, is prepared by distilling wine lees with seven or eight times their weight of water. It is the commercial "œnanthic ether," but is in reality a

mixture of various ethers of several of the higher fatty acids, and is used for flavouring poor quality brandies made from corn, spirit, etc., and for flavouring various liqueurs, etc. The artificial oil is easily made from the ethyl ethers of œnanthylic, caprylic and capric acids. Œnanthylic ether $CH_3(CH_2)_5 . CO_2C_2H_5$ is a liquid boiling at 188°. Caprylic ether $CH_3(CH_2)_6CO_2 . C_2H_5$ boils at 207° to 208°, and capric ether $CH_3(CH_2)_8 . CO_2C_2H_5$ boils with decomposition between 240° and 245°. The ethers prepared from the fatty acids of cocoanut oil, which include caprylic, caproic, capric, lauric, myristic and palmitic acids, are used as a basis for cognac essence.

The researches of Ordonneau (*Comptes Rendus*, cii., p. 217) are of great importance, as they embrace an exhaustive examination of a sample of cognac twenty-five years old of very fine quality. He was able to identify the following bodies in this brandy, and from these results an excellent artificial cognac oil can be made, with modifications to suit individual tastes. He found in each 100 litres :—

Acetic aldehyde . .	3 grammes.	Amine bases . .	4 grammes.
Acetal . . .	35 „	Ethyl acetate . .	35 „
Butyl alcohol . .	218·6 „	Propyl alcohol . .	40 „
Hexyl alcohol . .	1·5 „	Amyl alcohol . .	88·6 „
Propionic, butyric and caproic ethers .	3 „	Œnanthic ether . .	4 „

At the same time, it must be remembered that these results are exceptional, and the ordinary cognac oil is chiefly composed of ethers, the most important being œnanthic ether.

Artificial oils of almond (benzaldehyde and nitrobenzene), cassia (cinnamic aldehyde), wintergreen (methyl salicylate), garlic (allyl sulphide), and mustard (allyl isothiocyanate) have already been described under their respective oils. These are all chemical individuals, and may be called true synthetic oils, and in this respect differ from many of the

above-mentioned "artificial oils". The former are definite bodies of definite characteristics, whereas the latter are mixtures of several odorous constituents, which vary in proportions in the different brands on the market, and with a supply of the more common aromatic alcohols, esters and other bodies, the intelligent perfumer can reproduce very fairly many of the natural perfumes. At the same time it should be remembered that it is an almost general rule that the artificial perfumes have usually a harsher and less delicate odour than the natural ones, and in some cases are only very poor substitutes. In certain cases, however, this is not so, and an almost unlimited field of research exists in the chemistry of perfumes with a view to their synthetic production. Regard, however, should be paid, not only to the main odorous constituent of a given perfume, but also to the traces of other bodies which exist, and which modify the odour to that extent which determines the difference between the artificial and the natural perfume. When more attention is paid to this point, the artificial product will more closely resemble the natural body. As examples, one may quote *pure* benzaldehyde and *pure* cinnamic aldehyde. These cannot be mistaken by an expert nose for natural oils of almond and cassia respectively. Some traces of other odorous bodies are missing, and to such traces of bodies existing in essential oils great attention should be paid.

Caraw.		
Chamomile .	0·905-0·915.	+10° . —
Chenopodium . .	—	Sp. gr. = 0·965 - 0·985. Soluble in 5 volumes of 70 % alcohol. Laevo-rotary to −5°.
Cherry Laurel . .	—	—
Cinnamon . . .	Sp. gr. = 1·025-1·085. Minimum of 50 % of aldehydes.	Sp. gr. = 1·045 - 1·055. Aldehydes at least 75 %. Rotation not more than +1° or −1°. Soluble in 2 volumes of 70 % alcohol.
Citron	—	—
Clove	Sp. gr. not below 1·050.	Sp. gr. = 1·040 - 1·060. Soluble in 2 volumes of 70 % alcohol.
Copaiba . . .	Sp. gr. = 0·900-0·910. Laevo-rotary. Soluble in an equal volume of absolute alcohol.	Sp. gr. = 0·895-0·905. Laevo-rotary.
Coriander . . .	Sp. gr. = 0·870-0·885. Soluble in 3 volumes of 70 % alcohol.	Sp. gr. = 0·863-0·878. Soluble in 3 volumes of 70 % alcohol. Rotation +7° to +14°.
Cubebs . . .	Sp. gr. = 0·910-0·930.	Sp. gr. = 0·905 - 0·925. Rotation −25° to −40°.

APPENDIX II.

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Acacia Oil . .	Acacia cavenia (flowers)	—	—	—	Eugenol (40 to 50%); methyl eugenol; methyl salicylate (8%); benzyl alcohol (20%); benzaldehyde, geraniol; anisic aldehyde, and probably also linalol, decyl-aldehyde and ionone.
	Acacia faresiana (flowers)	—	—	—	Similar to above, but eugenol is absent. Farnesol.
Achillea Oil . .	Achillea coronopifolia (flowering herb)	0·924	—	—	—
Ajowan Oil . .	Ptychotis ajowan (fruit)	·900-·930	Dextro-rotary	—	Thymol; cymene; a terpene.
Almond Oil (bitter)	Amygdalus communis (fruit)	1·045-1·070	Inactive	1·542-1·5510	Benzaldehyde C_6H_5COH; prussic acid HCN; phenyl oxaceto-nitrile.
Ammoniacum Oil .	Dorema ammoniacum (resin)	·890	Dextro-rotary	—	—
Angelica Oil . .	Angelica officinalis (root)	·860-·905	+18° to +30°	1·4800	Phellandrene $C_{10}H_{16}$; methyl-ethyl-acetic acid; oxypenta-decylic acid.
Angostura Oil .	Galipea cusparia (bark)	·930-·960	−36°	—	Galipol $C_{15}H_{26}O$; cadinene $C_{15}H_{24}$; galipene $C_{15}H_{24}$.
Aniseed Oil . .	Pimpinella anisum (fruit)	·980-·990	0° to −2°	1·552-1·558	Anethol $C_{10}H_{12}O$; methyl chavicol $C_{10}H_{12}O$; anisic aldehyde $C_8H_8O_2$; anisic acid · anise ketone $C_{10}H_{12}O_2$ (?).

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Aniseed Oil (Star) .	Illicum verum (fruit) .	·980-·990	0° to – 2°	1·552-1·558	ANETHOL $C_{10}H_{12}O$; methyl chavicol $C_{10}H_{12}O$; anise aldehyde; anisic acid; ethyl hydroquinone; safrol; pinene $C_{10}H_{16}$; phellandrene $C_{10}H_{16}$.
Arnica Oil . .	Arnica montana (root) .	·990-1·000	– 1° to – 2°	—	Phlorone isobutyric ether $C_{16}H_{26}O_2$; thymo-hydroquinone; dimethyl ether $C_{12}H_{18}O_2$; phlorone dimethyl ether $C_{10}H_{14}O_2$; esters; hydrocarbons.
Asafœtida Oil . .	Ferula species (resin) .	·975-·990	– 10°	—	$C_7H_{14}S_2$; $C_{10}H_{20}S_2$; $C_8H_{16}S_2$; $C_{10}H_{18}S_2$; $C_{10}H_{16}O$; terpenes; sesquiterpene.
Asarum Oil . .	Asarum Europæum (root)	1·015-1·070	—	—	Asarone $C_{12}H_{16}O_3$; pinene $C_{10}H_{16}$; methyl eugenol $C_{11}H_{14}O_2$.
Asarum Oil . .	Asarum canadense (root)	·930-·960	—	—	Terpene; asarone $C_{12}H_{16}O_3$; esters; methyl eugenol $C_{11}H_{14}O_2O$.
Backhousia Oil .	Leaves of B. citriodora	0·895	0° to – 1°	—	Aldehydes 95% (chiefly citral); sesquiterpenes (traces); an amyl ester (?).
Bay Oil . . .	Pimenta acris (leaves) .	·965-·995	– 0° 30′ to – 2°	1·487-1·585 (increases with sp. gravity)	EUGENOL $C_{10}H_{12}O_2$; pinene $C_{10}H_{16}$ (?); dipentene $C_{10}H_{16}$; methyl eugenol $C_{11}H_{14}O_2$; phellandrene $C_{10}H_{16}$; hydrocarbon $C_{10}H_{16}$; chavicol $C_9H_{10}O$; methyl chavicol $C_{10}H_{12}O$; citral $C_{10}H_{16}O$.
Bay Oil (Californian)	Laurus Californica (leaves)	·930-·950	—	1·4785	Cineol $C_{10}H_{18}O$; terpineol $C_{10}H_{18}O$ (?).

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Bergamot Oil . .	Citrus bergamia (fruit) .	·882-·886	+8° to +20°	1·465-1·4700	Limonene $C_{10}H_{16}$; linalol $C_{10}H_{18}O$; linalyl acetate $C_{12}H_{20}O_2$; bergaptene $C_{12}H_8O_4$
Betel Oil . .	Piper betle (leaves) .	·953-1·045	−2° to +3°	—	Methoxy-chavicol $C_{10}H_{12}O_2$; cadinene $C_{15}H_{24}$; chavicol $C_9H_{10}O_2$.
Boldo Oil . .	Peumus boldus (leaves)	0·876	−4° to −6°	—	Eugenol (?); pinene; cuminal; acetic esters; an oxygenated body; a sesquiterpene.
	(dried leaves)	0·915-0·945	−2°	—	
Buchu Oil . .	Barosma species . .	·940-·945	—	1·4800	Diosphenol $C_{10}H_{16}O_2$; ketone $C_{10}H_{18}O$; hydrocarbon $C_{10}H_{18}$.
Cajuput Oil . .	Melaleuca species (leaves)	·917-·930	0° to −3°	1·460-1·4660	Cineol $C_{10}H_{18}O$; terpineol $C_{10}H_{18}O$; terpinyl esters; butyric, valeric and benzoic aldehydes; pinene $C_{10}H_{16}$ (?)
Calamus Oil . .	Acorus calamus (rhizome)	·960-1·000	+10° to +35°	1·507-1·515	Terpenes; sesquiterpene; oxygenated bodies not identified.
Camphor Oil . .	Camphora officinalis (wood and root)	—	—	—	Camphor $C_{10}H_{16}O$; safrol $C_{10}H_{10}O_2$; pinene $C_{10}H_{16}$; phellandrene $C_{10}H_{16}$; cineol $C_{10}H_{18}O$; eugenol $C_{10}H_{12}O_2$; cadinene $C_{15}H_{24}$.
Canella Oil . .	Canella alba (bark) .	0·922	—	—	Pinene; caryophyllene; cineol; eugenol.
Caparrapi Oil . .	Nectandra caparrapi .	·915-·925	−3°	—	Caparrapiol $C_{15}H_{26}O$; an acid $C_{15}H_{28}O_2$.
Caraway Oil . .	Carum carui (seed) .	·905-·920	+70° to +85°	1·487-1·497	Carvone $C_{10}H_{14}O$; limonene $C_{10}H_{16}$.

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Cardamom Oil .	Elettaria cardamomum (fruit)	·936-·946	+34° to +47°	1·460-1·470	Cineol $C_{10}H_{18}O$; terpineol $C_{10}H_{18}O$; acetic esters; limonene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$.
CardamomOil (Bengal) . . .	Amomum aromaticum (fruit)	·920	−12° 41′	1·4650	—
CardamomOil(Kameroon) . . .	Amomum danielli (fruit)	·907	−20° 34′	1·4655	—
Cardamom Oil(Siam)	Amomum cardamomum (fruit)	·905	+38° 4′	1·4639	Borneol $C_{10}H_{18}O$; camphor $C_{10}H_{16}O$; bornyl esters.
Carrot Oil . .	Daucus carota (seed) .	·870-·930	−18° to −40°	—	Pinene $C_{10}H_{16}$; terpineol $C_{10}H_{18}O$; cineol $C_{10}H_{18}O$.
Cascarilla Oil . .	Croton eleutheria (bark)	·890-·930	+5°	1·4930	Terpenes.
Cassia Oil . .	Cinnamomum cassia .	1·050-1·065	+1° to −1°	1·585-1·605	Cinnamic Aldehyde C_9H_8O; terpenes; cinnamic esters; o-methyl-coumaric aldehyde $C_{10}H_{10}O_2$.
Cedar Oil . .	Juniperus virginiana (wood)	·940-·960	−25° to −40°	1·493-1·503	Cedrene $C_{15}H_{24}$; cedrol $C_{15}H_{26}O$.
Cedar-leaf Oil . .	Juniperus virginiana (leaves)	·883-·888	+55° to +65°	—	Limonene $C_{10}H_{16}$; cadinene $C_{15}H_{24}$; borneol $C_{10}H_{18}O$; and bornyl esters.
Celery Oil . .	Apium graveolens (seed)	·870-·895	+65° to +80°	—	Limonene $C_{10}H_{16}$; sedanolic acid $C_{12}H_{20}O_3$; Sedanolide $C_{12}H_{18}O_2$; sedanonic acid $C_{12}H_{18}O$; sesquiterpene; guaiacol; palmitic acid.
Chamomile Oil (Roman) . . .	Anthemis nobilis (flowers)	·905-·915	—	1·4455	Esters of tiglic and angelic acids $C_5H_{20}O_2$ (chiefly amyl and hexyl); isobutyl isobutyrate $C_8H_{16}O_2$; esters of an alcohol, anthemol $C_{10}H_{18}O$.

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Chamomile Oil (German)	Matricaria chamomilla (flowers)	·930-·940	—	—	Esters of caproic acid $C_6H_{12}O_2$; hydrocarbons.
Champaca Oil (see Guaiacum-wood Oil)	Flowers of Michelia champaca (Java)	0·914	−13·25°	—	Benzoic acid or a benzoate.
	Flowers of Michelia champaca (Manila)	0·938	−54·1°	—	—
	Flowers of Michelia longifolia (Java)	0·883	−12·8°	—	—
Cheken-leaf Oil	—	·880	+20°	—	Pinene $C_{10}H_{16}$; Cineol $C_{10}H_{18}O$.
Chenopodium Oil	Artemisia absinthium (fruit)	·900-·975	−5° to −18°	—	—
Cherry-bark Oil (wild)	Prunus virginiana (bark)	1·050	Inactive	—	Benzaldehyde C_6H_5COH; prussic acid HCN.
Cherry-laurel Oil	Prunus laurocerasus (leaves)	1·050-1·065	Inactive	—	Benzaldehyde C_6H_5COH; prussic acid HCN.
Cinnamon Oil	Cinnamomum Zeylanicum (bark)	1·025-1·035	0° to −1°	1·590-1·599	Cinnamic aldehyde C_9H_8O; phellandrene $C_{10}H_{16}$; eugenol $C_{10}H_{12}O_2$.
Cinnamon-leaf Oil	Cinnamomum Zeylanicum (leaves)	1·045-1·060	−1° to +1°	1·5350	Eugenol $C_{10}H_{12}O_2$; cinnamic aldehyde C_9H_8O; safrol $C_{10}H_{10}O_2$.
Citronella Oil	Cymbopogon nardus (grass)	·885-·920	−0° 30′ to −16°	1·480-1·488 Java and Singapore oil = 1·4650-1·4680	Citronellal $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$; borneol $C_{10}H_{18}O$; methyl heptenone $C_8H_{14}O$; camphene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$.
Citron Oil	Citrus medica (peel of fruit)	·860-·870	+66° to +76°	1·4750	Limonene $C_{10}H_{16}$; citral $C_{10}H_{16}O$.

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Clove Oil . .	Eugenia caryophyllata (buds)	1·049-1·065	0° to −1° 30′	1·530 1·535	Eugenol $C_{10}H_{12}O_2$; carophyllene $C_{15}H_{24}$; amyl methyl ketone $C_5H_4O_2$; acet-eugenol (?).
Cognac Oil . .	From wine . . .	0·876-0·883	−0·C5° to +0·75°	—	Oenanthylic and other ethers; and aldehydes.
Conium Oil . .	Conium maculatum (fruit)	0·881	−2·2°	—	—
	Herb of C. maculatum .	0·931 at 20°	—	—	—
Copaiba Oil . .	Oleo-resin of Copaifera Lansdorfii and othe. species	0·900-0·910	−5° to −35°	—	Chiefly sesquiterpenes.
Coriander Oil . .	Coriandrum sativum (seed)	·870-·885	+7° to +14°	1·4665	Linalol $C_{10}H_{18}O$; pinene $C_{10}H_{16}$.
Costus Oil . .	Aplotaxis lappa (root) .	·980-·987	+15° to +16°	—	—
Cubeb Oil . .	Piper cubeba (fruit) .	·910-·930	−30° to −40°	1·490-1·496	Cadinene $C_{15}H_{24}$; dipentene $C_{10}H_{16}$; cubeb camphor $C_{10}H_{16}O$.
Culilaban Oil . .	Cinnamomum culilavan (fruit)	1·050	—	—	Eugenol $C_{10}H_{12}O_2$; methyl eugenol $C_{11}H_{14}O_2$.
Cumin Oil . .	Cuminum cyminum (fruit)	·890-·930	+4° to +6°	—	Cymene $C_{10}H_{14}$; cumic aldehyde $C_{10}H_{12}O$.
Cypress Oil . .	Cypressus sempervirens (leaves)	0·882-0·887	+4° to +6°	—	d-Pinene; l-cadinene; furfural; d-camphene; d-sylvestrene; cymene; a ketone; sabinol; acetate of d-terpineol (m.-pt. 35°); valeric acid; cypress camphor.
Dill Oil . . .	Anethum graveolens (fruit)	·900-·920	+70° to +80°	1·480-1·4950	Carvone $C_{10}H_{14}O$; limonene $C_{10}H_{16}$; a paraffin hydrocarbon.

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Dill Oil (East Indian)	Anethum Sowa (fruit) .	·970	+40°	—	Carvone $C_{10}H_{14}O$; limonene $C_{10}H_{16}$; dill apiol $C_{12}H_{14}O_4$.
Dog-fennel Oil .	Eupatorium feoniculaceum (herb)	·935	+18°	—	Phellandrene $C_{10}H_{16}$.
Elecampane Oil .	Inula pelenium (root) .	—	—	—	Alantic acid (C_6H_8O); alantolactone; alantol.
Elemi Oil . .	Oleo-resin of Manila Elemi of uncertain botanical origin	0·870-0·910	+45°	—	Phellandrene; dipentene; the higher fractions probably containing polyterpenes and oxygenated compounds.
Eriodictyon Oil .	Leaves of E. Californiana	0·937	−1·6°	—	Limonene; terpineol and esters.
Eucalyptus Oils (leaves)					
— Amygdalina .	—	·855-·890	−25° to −89°	1·4735	Phellandrene $C_{10}H_{16}$; cineol $C_{10}H_{18}O$.
— Backhousia .	—	·895-·902	—	—	Citral $C_{10}H_{16}O$; phellandrene $C_{10}H_{16}$.
— Baileyana . .	—	·890-·920	—	—	Cineol $C_{10}H_{18}O$; citral $C_{10}H_{16}O$; phellandrene $C_{10}H_{16}$.
— Capitallata .	—	·915	—	—	Cineol $C_{10}H_{18}$; eudesmol.
— Cneorifolia .	—	·915-·925	−5° to +5°	—	Cineol $C_{10}H_{18}O$; cumic aldehyde $C_{10}H_{12}O$.
— Corymbosa .	—	·880	—	—	Citral $C_{10}H_{16}O$ (?); geraniol $C_{10}H_{18}O$ (?) cineol; $C_{10}H_{18}O$.
— Crebra . .	—	—	—	—	Cineol $C_{10}H_{18}O$.
— Dealbata . .	—	·885-·900	—	—	Citronellal $C_{10}H_{18}O$; citronellol $C_{10}H_{20}O$.
— Dextro-pinea .	—	·873-·876	Dextro-rotary	1·4668	Dextro-pinene $C_{10}H_{16}$; aldehydes.
— Dumosa . .	—	·900-·912	—	—	Cineol $C_{10}H_{18}O$.

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Eucalyptus Oils (leaves)					
— Eugenoides .	—	·905-·910	+4° to +6°	—	Cineol $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$.
— Globulus . .	—	·910-·930	+1° to +10°	1·460-1·4670	Cineol $C_{10}H_{18}O$; pinene $C_{10}H_{16}$; ethyl alcohol C_2H_6O; amyl alcohol $C_5H_{12}O$; butyric, caproic and valeric aldehydes.
— Goniocalyx .	—	·915-·920	—	—	Cineol $C_{10}H_{18}O$.
— Gracilis . .	—	—	—	—	Cineol $C_{10}H_{18}O$.
— Hæmostoma .	—	·880-·890	—	—	Cymene $C_{10}H_{14}O$; cumic aldehyde $C_{10}H_{12}O$.
— Incrassata . .	—	—	—	—	Cineol $C_{10}H_{18}O$.
— Laevo-pinea .	—	·873	Laevo-rotary	1·4679	LAEVO-PINENE $C_{10}H_{16}$.
— Leucoxylon .	—	·920-·925	—	—	Cineol $C_{10}H_{18}O$.
— Loxophleba .	—	·883	+5°	—	Cineol $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$; aldehydes.
— Macrorhyncha .	—	·927	—	—	Cineol $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$: esters: eudesmol.
— Maculata var. Citriodora .	—	·870-·905	0° to +2°	—	Citronellal $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$.
— Microcorys .	—	·895-·930	—	—	Cineol $C_{10}H_{18}O$.
— Obliqua . .	—	·895-·915	−7°	—	Cineol $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$.
— Odorata . .	—	·900-·925	—	—	Cineol $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$; cumic aldehyde $C_{10}H_{12}O$.
— Oleosa . .	—	·905-·930	−5° to +5°	—	Cineol $C_{10}H_{18}O$.
— Planchoniana .	—	·915	—	—	Citronellal $C_{10}H_{18}O$.

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Eucalyptus Oils (leaves)					
— Populifolia . .	—	—	—	—	Cineol $C_{10}H_{18}O$; cumic aldehyde $C_{10}H_{12}O$.
— Punctata . .	—	·912-·921	−8° to +5°	—	Cineol $C_{10}H_{18}O$.
— Resinifera . .	—	·900	−15° to −20°	—	Cineol $C_{10}H_{18}O$.
— Risdonia . .	—	·910-·925	−2° to −6°	—	Cineol $C_{10}H_{18}O$; phellandrene $C_{10}H_{16}$.
— Rostrata . .	—	·915-·930	−2° to +13°	—	Cineol $C_{10}H_{18}O$; valeric aldehyde $C_5H_{10}O$.
— Stargeriana .	—	·880	—	—	Citral $C_{10}H_{16}O$.
Fennel Oil . .	Foeniculum vulgare (fruit)	·930-·980	+6° to +20°	1·525-1·534	Pinene $C_{10}H_{16}$; phellandrene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$; limonene $C_{10}H_{16}$; fenchone $C_{10}H_{16}O$; anethol $C_{10}H_{12}O$.
Feverfew Oil . .	Pyrethrum parthenium (flowers)	·900-·960	—	—	Borneol $C_{10}H_{18}O$ and its esters.
Fir-cone Oil . .	Abies excelsa (cones) .	·860-·875	−20° to −80°	—	Pinene $C_{10}H_{16}$; limonene $C_{10}H_{16}$; bornyl acetate $C_{12}H_{20}O_2$ (1 to 2 %).
Fleabane Oil . .	Eregeron canadense (herb)	·850-·890	+50°	—	Limonene $C_{10}H_{16}$; terpineol $C_{10}H_{18}O$.
Galangal Oil . .	Alpinia galanga (rhizome)	·915-·925	−1° to −4°	1·4900	Cineol $C_{10}H_{18}O$.
Galbanum Oil .	Peucedanum galbaniflorum (resin)	·910-·940	−5° to +20°	—	Pinene $C_{10}H_{16}$; cadinene $C_{15}H_{24}$.
Gardenia Oil . .	Fresh flowers . .	1·009	+3·0°	—	Benzyl acetate; styrolyl acetate; linalol; linayl acetate; terpineol; methyl anthranilate; esters of benzoic acid.

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Garlic Oil . .	Allium sativum (herb).	1·052	Inactive	—	Allyl-propyl-disulphide $C_6H_{12}S_2$; diallyl disulphide $C_6H_{10}S_2$; $C_6H_{10}S_2$: $C_6H_{10}S_2$.
Geranium Oil . .	Pelargonium species (herb)	·888-·905	−6° to −16°	1·460-1·471	Geraniol $C_{10}H_{18}O$; citronellol $C_{10}H_{20}O$; and tiglic acid esters.
Geranium Oil (Indian) . . .	Cymbopogon Martini (grass)	·885-·896	+2° to −2°	1·485-1·492	Geraniol $C_{10}H_{18}O$; geranyl esters; dipentene $C_{10}H_{16}$; methyl heptenone $C_8H_{14}O$ (?)
Ginger Oil . .	Zingiber officinale (rhizome)	·872-·885	−25° to −45°	1·488-1·4950	Phellandrene $C_{10}H_{16}$; camphene $C_{10}H_{16}$; sesquiterpene.
Ginger-grass Oil .	—	0·930-0·945	+18° to +27°	1·4850 (about)	Geraniol.
Golden-rod Oil .	Solidago canadensis and other species	·5)	−11° 10′	—	Terpenes; borneol $C_{10}H_{18}O$; bornyl acetate $C_{12}H_{20}O_2$; cadinene $C_{15}H_{24}$.
Grains of Paradise Oil	Amomum Melegueta (seeds)	·894	−4°	—	—
Guaiacum-wood Oil	Wood of guaiacum, species probably Bulnesia sarmentii	0·968 at 30° C.	−6·5 at 30° C.	—	Crystallisable guaiac alcohol $C_{14}H_{24}O$ or $C_{15}H_{26}O$, m.-pt. 91° C. ("Champacol[77]").
Gurjun Balsam Oil	Balsam of Dipterocarpus species	0·910-0·930	−35° to −106°	—	A sesquiterpene; small amounts of alcohols.
Hedeoma Oil (American)	Dried leaves and tops of Hedeoma pulegoides	0·925-0·940	+18° to +22°	—	Hedeomol ($C_{10}H_{18}O$); pulegone.
Hedychium Oil .	Hedychium corinarum (flowers)	·869	−0° 28′	—	—
Helichrysum Oil .	Helichrysum stoechas (herb)	·873	—	—	Pinene $C_{10}H_{16}$.
Hemp Oil . .	Cannabis sativa (herb) .	·930	−10° to 12°	—	Terpenes and sesquiterpenes.

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Hemp Oil (Indian)	Cannabis Indica (herb)	·930	—	—	Cannibene $C_{15}H_{24}$.
Heracleum Oil	Heracleum sphondylium (fruit)	·860-·880	Dextro-rotary	—	Octyl alcohol $C_8H_{18}O$; octyl acetate $C_{10}H_{20}O_2$; octyl caprate $C_{14}H_{28}O_2$; ethyl butyrate $C_6H_{12}O_2$.
Hop Oil	Humulus lupulus (flowers)	·840-·882	about +1°	1·4775	Humulene $C_{15}H_{24}$; geraniol $C_{10}H_{18}O$; tetrahydrocymene $C_{10}H_{18}$ (?); terpenes.
Hyssop	Hyssopus officinalis (herb)	0·925-0·940	−19° to −23°	—	Possibly thujone or thujyl alcohol.
Iva Oil	Dried flowering herb of Achillea moschate	0·932-0·934	—	—	Cineol; "ivaol," a mixture of oxygenated bodies of unknown constitution.
Jasmin Oil	Jasminum grandiflorum (flowers)	1·009-1·018	+2° 30′ to +3° 30′	—	Benzyl acetate $C_9H_{10}O_2$; linalyl acetate; jasmone; benzyl alcohol C_7H_8O; linalol $C_{10}H_{18}O$.
Juniper-berry Oil	Juniperus communis (berries)	·865-·900	−4° to −12°	1·4740-1·4880	Cadinene $C_{15}H_{24}$; pinene $C_{10}H_{16}$; an alcohol (m. pt. 165°) and its acetic esters.
Kaempferia Oil	Kaempferia rotunda (root)	·890-·900	+12°	—	Cineol $C_{10}H_{18}O$.
Kiku Oil	Pyrethrum Indicum (leaves)	·880-·890	—	—	—
Kuromoji Oil	Lindera sericea (leaves and twigs)	·890-·915	Laevo-rotary	—	Limonene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$; terpineol $C_{10}H_{18}O$; carvone $C_{10}H_{14}O$.
Laurel Oil	Laurus nobilis (leaves)	·920-·930	−15° to −18°	—	Pinene $C_{10}H_{16}$; cineol $C_{10}H_{18}O$.

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Lavender Oil . .	Lavendula vera (flowers)	·885-·900	−3° to −10°	1·462-1·4675	Linalyl acetate $C_{12}H_{20}O_2$ (English 7-10 %, French 25-40 %); pinene $C_{10}H_{16}$; limonene $C_{10}H_{16}$; geraniol $C_{10}H_{18}O$; sesquiterpene; cineol $C_{10}H_{18}O$ (in English oils).
Lemon Oil . .	Citrus limonum (peel) .	·857-·862	+59° to +65°	1·475-1·4775	Citral $C_{10}H_{16}O$; citronellal $C_{10}H_{18}O$ (?); limonene $C_{10}H_{16}$; geranyl and linalyl acetates $C_{12}H_{20}O_2$; phellandrene $C_{10}H_{16}$; stearoptene.
Lemon-thyme Oil .	—	0·898	−3°	—	Citral; thymol.
Lemon-grass Oil .	Cymbopogon citratus (grass)	·895-·905 (East Indian)	+3° to −3°	1·483-1·4880	Citral $C_{10}H_{16}O$; citronellal $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$; methyl heptenone $C_8H_{14}O$; esters and terpenes.
		0·877-0·887 (West Indian)	+2° to −2°	1·4875	
Lime Oil . .	Citrus limetta (fruit) .	·870-·875	+56° to +60°	1·4770	Linalyl acetate $C_{12}H_{20}O_2$; limonene $C_{10}H_{16}$; linalol $C_{10}H_{18}O$.
Lime Oil . .	Citrus medica var. Acida (expressed)	·873-·885	+35° to +40°	1·477-1·4800	Limonene $C_{10}H_{16}$; citral $C_{10}H_{16}O$; limettin $C_{11}H_{10}O_4$.
Lime Oil . .	Citrus medica var. Acida (distilled)	·856-·863	+40°	—	
Linaloe Oil . .	Bursera species . .	·872-·895	−4° to −13°	—	Linalol $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$; methyl heptenone $C_8H_{14}O$.
Lovage Oil . .	Levisticum officinale (roots)	1·005-1·045	+2° to +7°	—	Terpineol $C_{10}H_{18}O$.
Mace Oil . .	Myristica fragrans (arillus)	·880-·932	+10° to +20°	1·476-1·4840	Pinene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$; myristicol $C_{10}H_{16}O$; myristicin $C_{12}H_{14}O_3$; a phenol.

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Marjoram Oil	Origanum marjorana (herb)	·890-·910	+15° to +20°	1·475-1·485	—
Marjoram Oil (Cretic)	Origanum Smyrnaeum	·915-·966	0° to +15°	1·5100	Carvacrol $C_{10}H_{14}O$; linalol $C_{10}H_{18}O$; cymene $C_{10}H_{14}$.
Marsh-tea Oil	Ledum palustre (leaves)	·925-·935	—	—	Ledum camphor $C_{15}H_{26}O$.
Massoi-bark Oil	Massoia aromatica (bark)	1·040-1·060	—	—	Eugenol $C_{10}H_{12}O_2$; safrol $C_{10}H_{10}O_2$; pinene $C_{10}H_{16}$; limonene $C_{10}H_{16}$.
Masterwort Oil	Imperatoria ostruthium (root)	·875	—	—	Angelic aldehyde (?) C_5H_8O.
Matico Oil	Piper angustifolium (leaves)	·930-1·130	−1° to +6°	—	Asarone $C_{12}H_{16}O_3$; matico camphor $C_{12}H_{20}O$.
Meadow-sweet Oil	Spiræa ulmaria (herb)	—	—	—	Salicylic aldehyde $C_7H_6O_2$; terpene.
Melissa Oil	Melissa officinalis (herb)	·890-·925	+0° 30′ to −6° 30′	1·474-1·4840	Citral $C_{10}H_{16}O$; citronellal $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$; linalol $C_{10}H_{18}O$; citronellol $C_{10}H_{20}O$.
Mew Oil	Meum anthamanticum (root)	1·001	—	—	—
Mountain-mint Oil	Pycnanthemum incanum (herb)	·910-·940	+3° to +5°	—	Carvacrol $C_{10}H_{14}O$; pulegone $C_{10}H_{16}O$.
Musk-root Oil (sumbul)	Ferula sumbul (root)	·950-·965	—	—	—
Mustard Oil	Sinapis nigra (seeds)	1·014-1·032	0° to +1°	1·525-1·5350	Allyl thiocyanate C_3H_5CNS; carbon disulphide CS_2; cyanllyl.
Myrtle Oil	Myrtus communis (leaves)	·895-·920	+10° to +20°	—	Pinene $C_{10}H_{16}$; cineol $C_{10}H_{18}O$; dipentene $C_{10}H_{16}$ (?).
Myrtle Oil (bog)	Myrica gale (leaves)	·870	—	—	—

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Myrtle Oil (wax)	Myrica cerifera (leaves)	·885	−5°	—	—
Neroli Oil	Orange flowers	·870-·800	Dextro-rotary	1·4755	Limonene $C_{10}H_{16}$; linalol $C_{10}H_{18}O$; linalyl acetate $C_{12}H_{20}O_2$; methyl anthranilate $C_6H_4(NH_2)(CO_2CH_3)$.
Nigella Oil	Seeds of Nigella sativa	0·875	+1·5°	—	—
	Seeds of Nigella damascena	0·906	+1°	—	Damascenine $C_{10}H_{15}NO_3$.
Nutmeg Oil	Myristica fragrans (fruit)	·865-·920	+14° to +30°	1·4760	Terpenes; myristicol $C_{10}H_{16}O$ (?).
Olibanum Oil	Gum-resin of Boswellia Carberii and other species	0·875-0·885	−11·5°	—	Chiefly laevo-pinene; some phellandrene; dipentene; cadinene and oxygenated bodies.
Onion Oil	Allium cepa (herb and bulb)	1·035-1·045	−5°	—	Allyl-propyl-sulphide $C_6H_{12}O_2$.
Orange Oil	Citrus bigaradia (bitter) and Citrus aurantium (sweet)	0·847-0·853	+96° to +98° (sweet) +92° to +98° (bitter)	1·472-1·478	Limonene $C_{10}H_{16}$; citral $C_{10}H_{16}O$; citronellal $C_{10}H_{18}O$; a crystalline ester melting at 65°; methyl anthranilate.
Orange Oil (tangerine)	—	·859	+70°	—	Limonene $C_{10}H_{16}$; citral $C_{10}H_{16}O$; methyl anthranilate.
Origanum Oil (see Marjoram Oil).					
Orris Oil	Iris species (rhizome)	—	Dextro-rotary	—	Irone $C_{13}H_{20}O$; myristic acid $C_{14}H_{28}O_2$ and its methyl esters; oleic acid $C_{18}H_{34}O_2$; an oleic ester; oleic aldehyde $C_{18}H_{34}O$.
Paracoto Oil	—	0·925-0·950	−1° to −4°	—	Cadinene $C_{15}H_{24}$; methyl eugenol $C_{11}H_{14}O_2$.

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Paraley Oil . .	Petroselinum sativum (seeds)	1·050-1·100	−5° to −10°	1·4890	Apiol $C_{12}H_4O_{14}$; pinene $C_{10}H_{16}$.
Pastinic Oil . .	Pastinaca sativum (fruit)	·870-·890	Laevo-rotary	—	Ethyl alcohol C_2H_6O; octyl propionate $C_8H_{17}.C_3H_5O$; octyl butyrate $C_8H_{17}.C_4H_7O$.
Patchouli Oil . .	Pogostemon patchouli (leaves)	·975-·995	−50° to −68°	1·5115	Cadinene $C_{15}H_{24}$; patchouli camphor $C_{15}H_{26}O$.
Pechurim Oil . .	Nectandra puchury .	—	—	—	Esters of lauric and valerianic acids (?).
Peucedanum Oil .	Peucedanum grande (root)	·900	+30° to +35°	—	—
Pennyroyal Oil .	Mentha pulegium (herb)	·930-·960	+16° to +25°	1·4805	Pulegone $C_{10}H_{16}O$.
Pepper Oil . .	Piper nigrum (fruit) .	·870-·900	−5° to +2°	—	Terpenes; sesquiterpenes.
Peppermint Oil .	Mentha piperita (herb) .	·900-·920	−18° to −33°	1·4650	Menthol $C_{10}H_{20}O$; menthyl acetate $C_{12}H_{22}O_2$; and other bodies for which refer to text.
Peppermint Oil (Japanese)	Mentha arvensis (herb)	·895-·905	−25° to −43°	—	Similar to the above.
Persea Oil . .	Persea gratissima (leaves)	·960	+2°	1·5160	Methyl-chavicol $C_{10}H_{12}O$.
Petit-grain Oil .	Orange twigs and shoots	·885-·900	−2° to +5°	—	Limonene $C_{10}H_{16}$; linalol $C_{10}H_{18}O$; linalyl acetate $C_{12}H_{20}O_2$; geraniol $C_{10}H_{18}O$; geranyl acetate $C_{12}H_{20}O_2$; sesquiterpene.
Pimento Oil (Allspice)	Pimenta officinalis (fruit)	1·040-1·055	−1° to +4°	—	Eugenol $C_{10}H_{12}O_2$; sesquiterpene.
Pimpinella Oil .	Pimpinella saxifraga .	·960	—	—	—
Pine-needle Oil .	Pinus pumilio . .	0·859-0·865	−3° to −10°	—	—

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Poplar Oil . .	Populus nigra (buds)	·900-·905	—	—	—
Ragweed Oil . .	Ambrosia artemisifolia (herb)	·870	−26°	—	—
Rose Oil . . .	Rosa damascena (flowers)	0·853-0·858 at 30°	−1° to −4°	1·4580-1·4	Geraniol $C_{10}H_{18}O$; citronellol $C_{10}H_{18}O$; esters; paraffins; nerol; farnesol; phenyl-ethyl alcohol.
Rosemary Oil . .	Rosmarinus officinalis (flowering tops)	0·896-0·920	−9° to +18°	—	Borneol $C_{10}H_{18}O$; camphor $C_{10}H_{16}O$; bornyl acetate $C_{12}H_{20}O_2$; cineol $C_{10}H_{18}O$; camphene $C_{10}H_{16}$; pinene $C_{10}H_{16}$.
Rose-wood Oil . .	Convolvulus species (wood)	·900-·910	Lævo-rotary	—	Terpenes.
Rue Oil . . .	Ruta graveolens (herb) .	·832-·841	0° to +3°	—	Methyl-nonyl-ketone $C_{11}H_{22}O$; lauric aldehyde $C_{12}H_{24}O$.
Sage Oil . . .	Salvia officinalis (leaves)	0·910-0·930	+10° to +25°	—	Pinene $C_{10}H_{16}$; cineol $C_{10}H_{18}O$; borneol $C_{10}H_{18}O$; thujone $C_{10}H_{16}O$; sesquiterpene; esters.
Sage (Clary) Oil .	Salvia sclarea (leaves) .	0·907-0·928	−20° to −30°	—	Linalyl acetate (?).
Santal-wood Oil (East Indian)	Santalum album (wood)	0·973-0·985	−12° to −20°	1·505-1·510	Santalol $C_{15}H_{26}O$; an isomeric alcohol; santalal $C_{15}H_{24}O$; esters.
Santal-wood Oil (West Indian)	Amyris balsamifera (wood)	·950-·964	+10° to +30°	—	Amyrol $C_{15}H_{26}O$ (?).
Santal-wood Oil (West Aus.)	Santalum cygnorum (wood)	·945-·965	+5°	—	Santalol $C_{15}H_{26}O$ (?); esters.
Sassafras Oil . .	Sassafras officinale (wood)	1·065-1·095	+1° to +4°	—	Safrol $C_{10}H_{10}O_2$; pinene $C_{10}H_{16}$; phellandrene $C_{10}H_{16}$; camphor $C_{10}H_{16}O$; eugenol $C_{10}H_{12}O_2$; cadinene $C_{15}H_{24}$.

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Satureja Oil . .	Herb of Satureja thymbra	0·906	—	—	Cymol; thymol (19%); pinene; dipentene; bornyl acetate.
	Fresh herb of S. hortensis	0·898-0·924	+0·1°	—	Carvacrol (80%); cymene (?); pinene (?); traces of another phenol.
	Herb of S. montana (Mountain Savory)	0·939	+2·5°	—	Carvacrol; and, according to Haller, another phenol and a terpene.
Savin Oil . .	Juniperus sabina (twigs)	·910-·928	+40° to +60°	—	Pinene $C_{10}H_{16}$; cadinene $C_{15}H_{24}$; sabinol $C_{10}H_{16}O$; sabinyl acetate $C_{12}H_{18}O_2$.
Serpentaria Oil .	Rhizome and roots of Aristolochia serpentaria	0·975-0·988	−4°	—	Pinene; an ester of borneol; a body of the formula $C_{18} . H_{28}O$.
Shaddock Oil . .	Citrus decumanum (fruit)	·860	+90° to +95°	—	Limonene $C_{10}H_{16}$.
Silaus Oil . .	Silaus pratensis (fruit) .	·980-·990	Dextro-rotary	—	—
Snake-root Oil .	Asarum canadense .	0·930-0·960	—	—	—
Spearmint Oil .	Mentha viridis (herb) .	·920-·980	−30° to −50°	—	Carvone $C_{10}H_{14}O$.
Spice-wood Oil .	Laurus benzoin (bark).	·923	—	—	Methyl salicylate $C_8H_8O_3$; terpenes.
Spike Oil . .	Lavandula spica (flowers)	·905-·920	−3° to +7°	1·4660	Linalol $C_{10}H_{18}O$; cineol $C_{10}H_{18}O$; pinene $C_{10}H_{16}$; camphene $C_{10}H_{16}$; camphor $C_{10}H_{16}O$; borneol $C_{10}H_{18}O$; terpineol $C_{10}H_{18}O$; geraniol $C_{10}H_{18}O$.
Spoonwort Oil .	Fresh flowering plant of Cochlearia officinalis.	0·954	+55·5°	—	Secondary butyl thio-carbimide.
Sweet Birch Oil .	Bark of Betula lenta .	1·180-1·187	Inactive	—	Methyl-salicylate (99·8%); an ester and a paraffin, etc.

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Sweet Basil Oil .	Ocymum basilicum (herb)	·900	−20° to +12°	—	Methylchavicol $C_{10}H_{12}O$; linalol $C_{10}H_{18}O$; pinene $C_{10}H_{16}$; camphor $C_{10}H_{16}O$; cineol $C_{10}H_{18}O$.
Tansy Oil . .	Tanacetum vulgare (herb)	·925-·950	−25° to −35° (English) +30° to +45° (American)	—	Thujone $C_{10}H_{16}O$; borneol $C_{10}H_{18}O$; camphor $C_{10}H_{16}O$.
Tetranthera Oil .	Tetranthera citrata (fruit)	·920	—	—	Citral $C_{10}H_{16}O$.
Thuja Oil . .	Thuja occidentalis (leaves)	·910-·925	−6° to −15°	—	Thujone $C_{10}H_{16}O$; fenchone $C_{10}H_{16}O$; pinene $C_{10}H_{16}O$; traces of esters; carvone $C_{10}H_{14}O$.
Thyme Oil . .	Thymus vulgaris . .	·900-·950	Laevo-rotary	1·480-1·490	Thymol $C_{10}H_{14}O$; carvacrol $C_{10}H_{14}O$; menthone $C_{10}H_{18}$; linalol $C_{10}H_{18}O$; borneol $C_{10}H_{18}O$; cymene $C_{10}H_{14}$; bornyl acetate $C_{12}H_{20}O_2$; pinene $C_{10}H_{16}$.
Thyme (Wild) .	Dried herb of Thymus serphyllum	0·905-0·980	−1° to −11°	—	Thymol; carvacrol; cymene.
	Herb of T. camphoratus	0·904	—	—	Carvacrol (?).
	Herb of T. capitatus .	0·901	—	—	Pinene; cymene; dipentene; bornyl acetate; thymol; carvacrol (?).
Tuberose Oil . .	Flowers	—	—	—	A compound containing $C_{19}H_{20}O$.
Turmeric Oil . .	Curcuma longa (root) .	·940	Dextro-rotary	—	Turmerol $C_{10}H_{28}O$ (?); phellandrene $C_{10}H_{16}$.
Turpentine Oil (American)	Pinus species (wood) .	·855-·870	+10° to +15°	1·4700	—

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Turpentine Oil (French)	Pinus pinaster (wood) .	·855-·870	−18° to −40°	—	Pinene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$.
Turpentine Oil (German)	Pinus sylvestris (wood)	·860-·870	+15° to +20°	—	Pinene $C_{10}H_{16}$.
Turpentine Oil (Russian and Swedish)	Pinus ledebourdii (wood)	·870-·875	to +20°	—	Pinene $C_{10}H_{16}$; sylvestrene $C_{10}H_{16}$.
Valerian Oil . .	Valeriana officinalis (root)	·930-·960	−8° to −15°	—	Pinene $C_{10}H_{16}$; camphene $C_{10}H_{16}$; limonene $C_{10}H_{16}$; borneol $C_{10}H_{18}O$ and its esters; terpineol $C_{10}H_{18}O$; a sesquiterpene alcohol $C_{10}H_{20}O_2$.
Valerian Oil (Japanese)	Valeriana angustifolia .	·985-·995	−8° to −15°	—	Pinene $C_{10}H_{16}$; camphene $C_{10}H_{16}$; dipentene $C_{10}H_{16}$; terpineol $C_{10}H_{18}O$; borneol $C_{10}H_{18}O$ and its esters; a sesquiterpene kessyl acetate $C_{16}H_{26}O_2$.
Verbena Oil . .	Verbena officinalis .	·890-·900	−16° to +8°	—	Citral $C_{10}H_{16}O$.
Veti-vert Oil . .	Vetiveria zizanoides (grass)	1·010-1·030	+25° to +40°	—	—
Winter-green Oil .	Gaultheria procumbens (leaves)	1·177-1·187	0° to −1°	—	Methyl salicylate $C_8H_8O_3$, and traces of other bodies.
Winter-green Oil .	Betula alba (bark) .	1·180-1·187	Inactive	—	
Wormseed Oil .	Artemisia maritima .	·930-·935	—	—	Cineol $C_{10}H_{18}O$; dipentene $C_{10}H_{16}$ (?).
Worm-wood Oil .	Artemisia absinthium (herb)	·925-·955	—	1·460-1·470	Thujone $C_{10}H_{16}O$; thujyl alcohol $C_{10}H_{18}O$ and its esters; phellandrene $C_{10}H_{16}$; pinene $C_{10}H_{16}$.

APPENDIX II.—(*continued*).

Oil.	Source.	Specific Gravity at 15·5°.	Optical Rotation.	Refractive Index at 20°.	Constituents.
Ylang-Ylang Oil .	Flowers of Cananga odorata (East Indian)	0·930-0·950	−40° to −45°	—	Pinene; linalol; geraniol; iso-eugenol; linalyl and geranyl; acetates and benzoates; cadinene; a crystalline alcohol and paracresol methyl-ether.
	(Java)	0·910-0·940	−20° to −55°	—	
Zedary Oil . .	Curcuma zedoaria (roots)	·990-1·010	—	—	Cineol $C_{10}H_{18}O$.

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